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(11) Publication number: **0 480 469 A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **91117401.9**

(51) Int. Cl.⁵: **D21C 9/147, D21C 9/16,
D21C 9/153, D21C 9/14,
D21C 9/10**

(22) Date of filing: **11.10.91**

(30) Priority: **12.10.90 US 596765
03.10.91 US 770628**

(43) Date of publication of application:
15.04.92 Bulletin 92/16

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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(54) **Chlorine-free wood pulps and process of making.**

(57) This invention provides for a batch and continuous process with countercurrent recycle of bleaching filtrates for the delignification and bleaching of pulp. Oxygen delignification of pulp is achieved in excess of 50% as measured by kappa numbers, while the pulp viscosity is minimally decreased by no more than about 8 cps. Bleaching of delignified pulp may be achieved with peroxy compounds and ozone and pulp brightness of from about 82 to 88 ISO may be achieved with pulp containing zero level TOX from chlorine based bleaching chemicals and zero level of AOX in the bleach effluents. Higher brightness of from about 90 to about 92 ISO can also be achieved by addition of very low levels of chlorine based bleaching chemicals. Corresponding bleach effluents contain less than 200 ppm AOX. Bleaching filtrates may be recycled for pulp washing and for use with an organosolv pulping process which results in significant energy savings and mitigation if not elimination of pollution typically associated with chlorine based bleaching. This invention also relates to bleach pulp product derived from the process and to an apparatus for carrying out the process.

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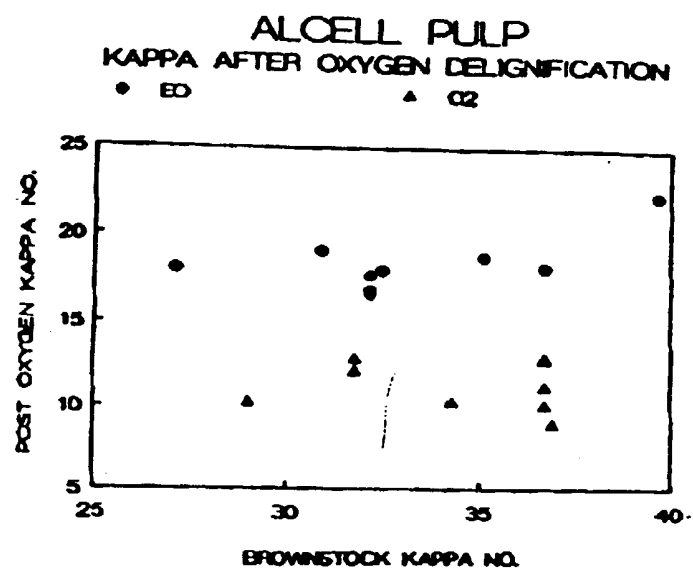


FIGURE 1

Cross-Reference to Related Application

This is a continuation-in-part of Application Serial Number 07/596,765 filed October 12, 1990.

5 Background of the Invention

In recent years, there has been increasing public concern about industrial waste streams, emissions, and solid wastes being discharged into the environment. Market and regulatory pressures are now requiring manufacturers in all industrial sectors to minimize this discharge burden on the environment.

10 In the pulp bleaching industry, effluents from pulp mill bleach plants have received public and government scrutiny. Such effluents contain chlorinated organic bleaching reaction products which are generally measured by their adsorbable organic halogen (AOX). Bleached pulp may also contain chlorinated organic residues which are generally measured by their total organic halogen (TOX).

Earl and Reeve, of the University of Toronto, have studied levels of AOX in bleach plant effluents, and 15 have developed an empirical relationship to predict AOX levels produced in the bleaching process. According to Reeve's group, AOX in bleach plant effluents will be about 10% of the weight of molecular chlorine (Cl_2), and 5.3% of the weight of chlorine dioxide (ClO_2) used in the bleaching process. Using the amounts of chlorine and chlorine dioxide that are customary to bleach softwood kraft pulps With "conventional" bleaching technology, AOX in untreated bleach plant effluents is found to be in the range of 20 5 to 8 kg AOX per ton of pulp bleached. Secondary treatment systems will remove an additional 40% to 60% of this AOX, indicating that the range of AOX discharged to receiving waters will be about 2 to 6.8 kg AOX per ton. Current regulatory targets seem to allow a maximum of about 2.5 kg AOX per ton, with further restrictions to 1.5 kg per ton in the foreseeable future.

The use of chlorine based bleaching chemicals additionally leaves some chlorinated organic residues in 25 the pulp. A recent study by Reeve's group has shown that total TOX in bleached softwood kraft pulps from Canadian mills (where few mills have oxygen delignification) is in the range of 400 to 600 parts per million (ppm), and that for bleached hardwood kraft pulps, values as high as 2,000 ppm have been determined.

Therefore, traditional pulp mills mostly of the kraft process type have devised new digestion conditions for increasing delignification of the wood pulp and have attempted to implement oxygen delignification prior 30 to bleaching in order to reduce the consumption of chlorine containing bleaching agents. Other attempts at oxygen delignification include the substitution of chlorine dioxide for molecular chlorine to give equivalent bleaching with much lower levels of atomic chlorine. The combination of these technologies should provide the means for kraft mills to meet the 1.5 kg AOX per ton limit.

On the other hand, new bleaching processes are being developed which contain no chlorine bleaching 35 chemicals. For conventional kraft softwood pulps, bleaching processes using oxygen, ozone and hydrogen peroxide have been developed. Softwood kraft pulps bleached with oxygen and hydrogen peroxide are of low brightness and have questionable strength properties. Other developments with kraft and sulfite pulping processes involve the incorporation of ozone bleaching equipment in an effort to eliminate the use of chlorine containing bleaching agents.

40 However, with kraft pulps which constitute the industry's standard for pulp strength for either hardwood or softwood species, lower brightness levels have been achieved as compared to brightness levels obtained with chlorine or chlorine dioxide as bleaching agents.

There are additional environmental and economic benefits from the use of non-chlorine bleaching agents including the recyclability of industrial waste streams. Furthermore, bleaching processes using non- 45 chlorine bleaching agents have the potential for disposal of all bleach plant residues by burning. Currently, bleaching processes which use oxygen delignification are able to recycle the bleach effluents from this stage to the mill chemical recovery system. The benefits that accrue include a reduced demand on secondary treatment systems and a decrease in chemical processing costs. Additionally, through recycle of effluents and discharge of cleaner industrial waste streams, the costs associated with industrial waste 50 treatment decrease. Therefore, it is advantageous to devise industrial processes which make use of recycled effluents, require less fresh water, and discharge less industrial waste all of which result in an overall decrease in plant operating costs.

Industrial processes which are designed with the foregoing objectives make use of the "Closed-Mill" concept. This concept requires that all process chemicals, including water, be recycled and also requires 55 that almost all waste, including heat is reused.

Wood pulps produced by organosolv pulping of lignocellulosic material such as described, for example, in U.S. Patent Nos. 4,100,016 and 4,764,596 also referred to as the ALCELL® process, employ alcohol extraction. Such processes will be collectively referred to as "organosolv processes" and offer some

distinct advantages for closing a pulp mill while providing commercial quality hardwood pulps that are comparable in strength, brightness and cleanliness to kraft pulps produced from the same wood species. In such processes, by the methods of the present invention, the bleach plant effluents can be returned to the pulp mill with minimal treatment.

5 For optimal pulp strength, however, organosolv pulps must be digested by cooking such that there is a higher residual lignin in the organosolv pulp as compared to kraft pulps. The pulp at this stage is referred to as brownstock and residual lignin in pulp brownstock is measured by units called kappa numbers. Typical kappa numbers for organosolv pulps are approximately 25 to 35, depending on the wood species and other factors, whereas kappa numbers for kraft hardwood pulps typically will vary between about 17 and 21, 10 depending on the same factors. The consequence of the higher kappa number in organosolv pulps is generally that larger quantities of bleaching chemicals must be used to produce bleached pulps at the same brightness level as compared to kraft pulps. However, as compared to kraft pulps, the methods of the present invention require smaller amounts of bleaching compounds, other than oxygen and sodium hydroxide, to achieve bleached pulps with similar brightness as measured by the standard of the 15 International Organization for Standardization (ISO).

Viscosity which is a measure of pulp strength (centipoise, cps, TAPPI Standard T-230) is also one of the important characteristics of pulp. Typical viscosities of organosolv pulp brownstock range from approximately 40 to 13 cps and those for kraft pulp brownstock range from about 45 to 20 cps, with the lower numbers indicating lower viscosity or strength. It is desirable to have as little decrease in viscosity as 20 possible during the bleaching process, since viscosity losses are usually associated with a decrease in pulp strength, as measured by customary tensile, burst and tear strength tests.

A disadvantage of the kraft process is that oxygen delignification of kraft pulp brownstock results in reduction of pulp strength below acceptable limits when oxygen delignification of the pulp exceeds a 50% of which corresponds to a reduction of the brownstock kappa number in excess of 50%.

25 By contrast, the methods of the present invention show that pulps can be bleached to above 85 ISO without the use of chlorine containing bleaching chemicals. The net result is that very low levels of adsorbable organic halogen (AOX) and total organic halogen (TOX) will be present in the bleach effluent and the bleached pulp respectively. Additionally, if a brightness above 85 ISO is required, it can be achieved with the use of low levels of chlorine dioxide such that the adsorbable organic halogen in the 30 untreated bleach plant effluent is approximately 0.5 kg AOX per ton of pulp.

Summary of the Invention

It is a primary object of this invention to provide a process for the oxygen delignification of pulp wherein 35 the pulp residual lignin is decreased in excess of 50% with little or no decrease in pulp viscosity.

It is another primary object of this invention to provide a process for oxygen delignification of pulp wherein the pulp residual lignin is decreased in excess of about 50% to about 76% with little or no decrease in pulp viscosity.

It is another object of this invention to provide a process for further delignification of the pulp with ozone 40 wherein the pulp residual lignin is decreased in excess of from about 80% to about 90% with little or no decrease in pulp viscosity to within about 2 to 5 cps.

It is another object of this invention to provide a process for bleaching the delignified pulp to a brightness in excess of about 70 ISO to about 88 ISO with no use of chlorine based bleaching chemicals.

It is another object of this invention to delignify and bleach organosolv pulps with relatively high kappa 45 values as compared to kraft pulps from the same wood species to a high brightness level and without loss of strength.

In one aspect of the invention, a process is provided for oxygen delignification of pulp wherein the pulp residual lignin is decreased in excess of 50% with little or no decrease in pulp viscosity.

In one aspect of the invention, a process is provided for oxygen delignification of pulp wherein the pulp 50 residual lignin is decreased in excess of about 50% to about 76% with little or no decrease in pulp viscosity.

In another aspect of this invention, a process is provided for enhancing the effect of oxygen delignification comprising pretreating pulp brownstock with a peroxy compound such as peracetic acid or hydrogen peroxide, prior to performing oxygen delignification.

55 In another aspect of this invention, a process is provided for enhancing the effect of oxygen delignification comprising pretreating pulp brownstock with ozone prior to performing oxygen delignification.

In another aspect of this invention, a process is provided for enhancing the effect of oxygen delignification comprising treating the delignified pulp with a peroxy compound such as peracetic acid or

hydrogen peroxide.

In another aspect of this invention, a process is provided for enhancing the effect of oxygen delignification comprising treating the delignified pulp with ozone.

In another aspect of this invention, a process is provided for enhancing the effect of oxygen delignification comprising pretreating pulp brownstock with ozone prior to performing oxygen delignification.

In yet another aspect of this invention, a process is provided for enhancing the effect of oxygen delignification comprising pretreating pulp brownstock with a peroxy compound prior to performing oxygen delignification, and treating the resulting pulp with a peroxy compound such as peracetic acid or hydrogen peroxide.

In yet another aspect of this invention, a process is provided for enhancing the effects of oxygen delignification comprising pretreating pulp brownstock with ozone prior to performing oxygen delignification, and treating the resulting pulp with a peroxy compound such as peracetic acid or hydrogen peroxide.

In still another aspect of this invention, a process is provided for enhancing the effect of oxygen delignification comprising performing oxygen delignification and treating the resulting pulp with two bleaching stages of either peracetic acid, hydrogen peroxide, or a combination of both peracetic acid and hydrogen peroxide.

In still another aspect of this invention, a process is provided for enhancing the effect of oxygen delignification comprising performing oxygen delignification and treating the resulting pulps with two bleaching stages of either peracetic acid, hydrogen peroxide and ozone, or a combination of both peracetic acid and hydrogen peroxide or ozone.

In another aspect of this invention, a continuous process is provided for the delignification and bleaching of pulp wherein bleaching filtrates are used to wash pulp brownstock and thereafter recycled for reuse in a continuous pulping process.

Other features and advantages of this invention will be apparent from the following description of the preferred embodiment and from the claims.

Description of the Drawings

Figure 1 is a graph showing the reduction in kappa numbers of ALCELL® pulps after oxygen delignification (O_2) (Δ) and after oxidative extraction (E_o) (o).

Figure 2 is a graph which compares the reduction in kappa numbers and viscosity values of ALCELL® and kraft pulps after oxygen delignification.

Figure 3 is a beating curve for an organosolv birch pulp bleached to 88 ISO with the sequence E_o DED.

Figure 4 is a beating curve for an organosolv birch/aspens/maple pulp bleached to 88 ISO with the sequence ODED.

Figure 5 is a beating curve for an organosolv birch/aspens/maple pulp bleached to 83 ISO with the sequence PO(PA)P.

Figure 6 is a flow chart of a process for the continuous delignification and bleaching of pulp brownstock using countercurrent washing and recycling of solvents and bleaching filtrates using the following sequences: (Peroxy)O(Peroxy)(Peroxy) and (Peroxy)OZ(Peroxy) wherein (Peroxy) is either hydrogen peroxide or peracetic acid.

Figure 7 is a flow chart of a process for the continuous delignification and bleaching of pulp brownstock using countercurrent washing and recycling of solvents and bleaching filtrates using the following sequences: ODE_oD and ODED.

Figure 8 is a flow chart of a process for the continuous delignification and bleaching of pulp brownstock using countercurrent washing and recycling of solvents and bleaching filtrates using the following sequences: O(Peroxy)D and OZD wherein (Peroxy) is either hydrogen peroxide or peracetic acid.

Detailed Description of the Preferred Embodiment

This invention generally relates to the delignification and bleaching of pulps obtained from kraft and organosolv pulping processes. The delignification and bleaching steps of the process can be carried out in either a batch or continuous mode. Pulps can be delignified with oxygen and bleached, and Kappa values can be decreased in excess of 50% and preferably in the range of from about 50% to about 76% without any significant decrease in pulp viscosity. Commercially acceptable high brightness levels can also be achieved. The bleaching effluent streams from the practice of the present invention meet or exceed stringent environmental regulations.

By either the batch or continuous processes of the invention, oxygen delignification of organosolv pulps

yield a reduction of kappa numbers in excess of about 50% and preferably up to about 76% and without a decrease in viscosity values of no more than about 8 cps., preferably within about 2 to about 5 cps.

Figure 1 shows that an organosolv pulp such as ALCELL® pulp with an initial kappa number of 29 can be delignified using oxygen to a kappa number of about 10, an approximately 67% delignification. As shown however in Figure 2 by closed circles, the viscosity of the ALCELL® pulp is essentially unchanged with increased delignification. By contrast, a kraft softwood brownstock, shown by open circles in Figure 2, shows a linear viscosity decrease with increasing delignification, as reported by others. Generally, kraft hardwood pulps manifest a similar decrease in viscosity with oxygen delignification. At an approximately 50% delignification, the pulp viscosity decreases to a point wherein further delignification would begin to seriously impact the pulp strength properties. Figure 2 further shows that the kappa number of oxygen delignified pulp is relatively independent of the brownstock kappa number, and that the final kappa number is in the range of about 9 to about 13 for oxygen delignification. The final kappa number for pulp delignified by oxidative extraction, which provides milder reaction conditions, is in the range of from about 16 to 18.

With reference to the beating curves of Figures 3, 4 and 5, it can be seen that strength properties for organosolv pulps are comparable to those of kraft pulps or the same wood species. The beating curves are PFI mill beating curves and are obtained according to TAPPI Standard 248 OM-85. The physical properties shown on the curves are measured according to TAPPI Standards 220 OM-88, 403 OM-85, 414 OM-88 and 494 OM-88. The bleaching sequences used were analogous to those described in Examples 16, 14 and 19 respectively.

Furthermore, delignification and bleaching of pulps can be enhanced to achieve commercially acceptable brightness levels, again without significant viscosity loss, by contacting the pulp with either peracetic acid or hydrogen peroxide, either alone, in staged exposures, or in oxygen delignification followed with, and either before or after oxygen delignification. An ozone stage can also be used in combination with oxygen delignification, and either before or after hydrogen peroxide or peracetic acid. Here again, commercially acceptable brightness levels are achieved.

Generally, organosolv processes produce hardwood pulp fiber with residual lignin contents with typical kappa numbers of from about 20 to about 40. By the methods of the present invention, an organosolv pulp with a brownstock kappa number of about 40 can be delignified to a kappa number of about 10 in one treatment stage, a reduction of about 75%, with an oxygen stage alone. Alternatively, when the pulp is treated with ozone either before or after an oxygen delignification stage, the pulp is delignified to a kappa number of from about 80% to about 90%.

Treatment of the pulp brownstock with peroxy compounds such as hydrogen peroxide or peracetic acid in the range of from about 0.5% to about 4% (w/w) peroxy compound on oven dry (o.d.) pulp for either peracetic acid or hydrogen peroxide result in reduction of the kappa number after oxygen delignification by about an additional 50%, to a kappa number of about from 5 to about 7, as compared with the kappa number after a single oxygen delignification stage.

Pulps treated with either peracetic acid or hydrogen peroxide after oxygen delignification, either with or without pretreatment with a peroxy compound, show enhanced bleaching responses as compared with similarly treated kraft pulps. The results of pulp treatment with a peroxy compound after oxygen delignification is that fewer bleaching steps are required to reach a specific brightness level and lower amount of bleaching chemicals are required.

Enhanced bleaching responses are obtained when pulps are pretreated with a peroxy compound before oxygen delignification then are treated in one or more stages with a peroxy compound. A brightness of from about 83 to 86 ISO can be achieved which is in the same brightness range obtained when pulps have not been pretreated with peroxy compounds but have been treated with chlorine based bleaching chemicals. An added advantage is that these pulps contain zero level TOX from chlorine based bleaching chemicals and correspondingly the bleach effluents also contain zero level AOX.

Enhanced bleaching responses are also obtained when pulps are treated with ozone either before or after oxygen delignification followed by treatment with one or more peroxy stages. These pulps have a brightness of from about 82 to 86 ISO which is in the same brightness range obtained when pulps have not been treated with ozone but have been treated with chlorine based bleaching chemicals. Again, an added advantage is that these pulps contain zero level TOX from chlorine based bleaching chemicals and correspondingly the bleach effluents also contain zero level AOX.

Enhanced bleaching responses are obtained when pulps are treated in a continuous delignification and bleaching process with a peroxy compound before or after oxygen delignification and followed by a bleaching stage with either peroxy compound or ozone. A brightness of from about 83 to about 88 ISO can be obtained. Alternatively, when pulps are treated with a chlorine dioxide stage, a brightness value of from about 90 to about 92 ISO can be obtained.

Generally, before delignification or bleaching, pulp brownstock is washed with an alcohol solution comprising; from about 40 to about 80% (by volume) of a water miscible lower aliphatic alcohol of 1 to 4 carbon atoms (e.g., methanol, ethanol, isopropanol or tert-butanol); from about 20 to about 60% water; and if needed, a small amount of a strong water soluble acid, such as a mineral acid (e.g., hydrochloric, sulfuric, phosphoric or nitric acid) or an organic acid (e.g., oxalic acid, preferably acetic, formic or peroxy acids) to remove any soluble lignin prior to delignification or bleaching. The alcohol washed pulp is washed again with water to remove any residual alcohol and is delignified and bleached in either a batch or continuous mode.

Pulp brownstock can be treated with a peroxy compound, for example, using peracetic acid (PA) or hydrogen peroxide (P) at a pH of from about 1.5 to about 11, preferably at a pH of from about 2 to about 6 with peracetic acid (PA) or preferably at a pH of from about 8.5 to about 11 with hydrogen peroxide (P) and in an amount of from about 0.2 to about 2%, preferably from about 0.5 to about 1.5% (w/w) by weight of peroxy compound per weight of oven dried (o.d.) pulp. When hydrogen peroxide is used, the final pH is preferably from about 8.5 to about 11 and is maintained at such a level by addition of caustic. The pulp can be of any consistency of from about 8% to about 55%, but is preferably between about 10% to about 20%. The reaction time is from about 0.3 to about 3 hours and at a temperature of between about 40°C and about 90°C.

Alternatively, in conjunction with treatment with a peroxy compound, the pulp brownstock can also be treated in a separate step with transition-metal chelating agents in an amount of from about 0.05 to about 1% (w/w) metal chelating agent on oven dried (o.d.) pulp, for a reaction time period long enough to ensure chelation, for example using ethylenediamine tetraacetic acid (EDTA) or diethylene triamine pentaacetic acid (DTPA) in order to prevent catalytic decomposition of the peroxy compound by transition metal ions (such as manganese, copper, and iron). Treatment by transition-metal chelating agents can either be carried out preceding or during the peroxy compound treatment step. As an alternative to chelation, the pulp can also be first soured with a sulfurous acid (H_2SO_3) wash by washing the pulp with water through which sulfur dioxide (SO_2) gas is bubbled at a concentration such that the pH is from about 2 to about 3. As an alternative to sulfurous acid, mineral acids such as sulfuric acid can also be used. The soured pulp or the pulp pretreated with metal chelating agents is then subjected to a peroxy compound treatment. After peroxy compound treatment, the pulp is washed with water. Alternatively, if the next treatment step is oxygen delignification, the washing step may be omitted. Magnesium sulfate at from about 0.1% to about 1.0% (w/w) magnesium sulfate on oven dried (o.d.) pulp can also be added for viscosity protection of the pulp.

An ozone stage (Z) can be also be used to treat pulp brownstock either as a pretreatment prior to oxygen delignification (sequence ZO) or following oxygen delignification (sequence OZ). Pulp brownstock treatment with ozone is carried at a pH of from about 1.5 to about 5, preferably from about 2 to about 3 at a temperature of from about 20° to about 60° C, preferably 25° to about 30° C. The pH may be adjusted to the appropriate level using acid (e.g. acetic or sulfuric acid). Enough water is added or removed using known techniques that the pulp consistency is from about 10% to about 55%, preferably about 42%. A catalyst may be added, such as ethanol at a level of from about 0.5% to about 1%, preferably about 0.8% (w/w) ethanol on oven dried (o.d.) pulp. Ozone is generated using known techniques. When a high consistency pulp is used with from about 20 to about 50% pulp solids, the pulp is fluffed into separated fibers and the fibers are rapidly mixed with ozone gas at a concentration of from about 0.2% to about 2% (w/w) ozone on oven dried (o.d.) pulp. When a medium consistency pulp is used, ozone is introduced to the pulp either as an ozone containing solution or as a gas. Ozone solution is obtained from first pressurizing the ozone over water at an elevated pressure sufficient to dissolve enough ozone such that the concentration of ozone is from about 0.2% to about 2% (w/w) ozone on oven dried (o.d.) pulp after the ozone solution is mixed with the pulp. Any unreacted ozone can be removed as off-gas and can be monitored using known techniques. Subsequent to the ozone treatment stage, the pulp pH can be adjusted using caustic to a pH of from about 9 to about 11, then, if need be, the pulp can be further adjusted to a neutral pH by successive washing with water.

Alternatively, when an ozone stage is used following oxygen delignification (sequence OZ) of pulp brownstock, the same conditions are generally followed as in the preceding paragraph. However, following oxygen delignification, residual caustic in the pulp is washed from the pulp using water and the pH can be adjusted to a pH of from about 2 to about 5 by the addition of an acid.

Oxygen delignification (O) of brownstock pulp can generally be used either as a first stage (sequences OP, O(PA), OZ), or following a peroxy compound treatment stage or an ozone treatment stage (sequences PO, (PA)O, ZO). Oxygen delignification is conducted by mixing a pulp slurry of from about 9% to about 15%, preferably from about 10% to about 12% consistency by weight of pulp solids with a caustic solution including, for example, sodium hydroxide. The amount of caustic added is preferably between from about

2% to about 8%, more preferably from about 3% to about 6% (w/w) caustic on oven dry (o.d.) pulp. The pulp slurry thus obtained is further mixed at high shear with oxygen gas such that the weight of oxygen gas is from about 0.5% to about 2%, preferably from about 0.8% to about 1.5% (w/w) oxygen on oven dry (o.d.) pulp. The temperature of the reaction mixture is between from about 60°C to about 110°C, more preferably from about 70°C to about 90°C, and oxygen pressure is maintained between from about 30 to about 100 psig, more preferably between from about 80 to about 100 psig. The reaction time is between from about 6 to about 60 minutes, more preferably between from about 25 to about 45 minutes. Additional chemicals may be added to help preserve strength properties and include from about 0.1% to about 1% magnesium sulfate, from about 0.1% to about 0.5% diethylene triamine pentaacetic acid (DTPA), and from about 0.5% to about 3% sodium silicate.

Generally, an oxidative extraction stage (E_o) can also be used to delignify a pulp brownstock following a first peroxy compound bleaching stage, preferably following a peracetic acid first bleaching stage (sequence $O(PA)E_o$, $(PA)E_o$), an ozone bleaching stage (sequence OZE_o , ZE_o) or a first chlorine dioxide bleaching stage (sequence ODE_oD). An oxidative extraction stage can also be used before a first chlorine dioxide bleaching stage (sequence E_oDED). A pulp slurry is mixed at from about 9% to about 40%, preferably from about 10% to about 12% consistency by weight of pulp solids with a caustic solution of from about 2% to about 5%, preferably from about 2.5% to about 4% (w/w) sodium hydroxide on oven dry (o.d.) pulp. From about 0.1% to about 1% magnesium sulfate is added to the pulp mixture. Oxygen gas is introduced at from about 30 to about 100 psig, preferably at from about 30 to 60 psig and is mixed with the pulp at high shear and for a length of time sufficient to ensure appropriate mixing. The temperature of the reaction mixture is between from about 60°C to about 110°C, preferably between from about 70°C to about 90°C, and oxygen pressure is maintained between from about 30 psig to about 100 psig preferably between from about 30 to about 60 psig. The total reaction time with the oxygen is between from about 6 and about 60 minutes. For the first 10 to 15 minutes, the pressure of oxygen is decreased to atmospheric and the pulp then remains in an oxygen rich atmosphere for about 20 to about 40 minutes.

Generally, oxygen delignified pulp (O) can be treated with chlorine dioxide (D) as a subsequent first bleaching stage (sequence OD). An ozone-treated oxygen delignified pulp (sequence OZ) can also be treated with chlorine dioxide (sequence OZD) and an ozone treatment can also be used after a peroxy treatment stage (sequences OPD, $O(PA)D$). Chlorine dioxide is used in the range of from about 0.2% to about 1.5% (w/w) chlorine dioxide on oven dry (o.d.) pulp. The pulp consistency is from about 9% to about 15%, preferably from about 10% to about 12%. A bleaching stage with chlorine dioxide following oxygen delignification is carried forward at a final pH of from about 2 to about 3 and caustic may be added as need be to maintain the pH in this range. Treatment with chlorine dioxide proceeds at a temperature of from about 30° to about 70°C and for about 0.3 to about 3 hours, preferably 0.3 to 2 hours. Optionally, a second bleaching stage using chlorine dioxide may be used following an oxidative extraction stage (E_o) or a conventional alkaline extraction stage (E) on a first bleached pulp with chlorine dioxide (sequence ODE_oD , ODE_oD). An alkaline extraction stage consists of mixing the pulp brownstock with from about 0.5% to about 2% caustic, at a temperature of from about 40° to about 70°C and for about 1.5 to about 3 hours followed by washing with water to dissolve and remove any chlorine dioxide bleaching reaction products. Conditions are generally the same as in a chlorine dioxide first bleaching stage, however, a preferred final pH is from about 3.5 to about 4.5 which can be achieved by appropriate addition of caustic, and a preferred reaction time is between about 1.5 to about 2 hours.

Pulp brownstock can be delignified and bleached in a continuous mode. As shown in Figures 6, 7 and 8, bleaching filtrates obtained from a subsequent bleaching or delignification stage can be recycled as wash water for pulp brownstock washing at an earlier stage. Furthermore, after pulp brownstock washing, these bleaching filtrates can be mixed with water and can become part of the alcohol/water solvent used in a continuous organosolv pulping process such as described in U.S. Patent Application Serial No. 07/649,683 or to precipitate the lignin in such a process. In another alternative, these bleaching filtrates can also be concentrated, preferably by evaporation to produce evaporator condensate and such evaporator condensate can be used as wash water for pulp brownstock washing as described above. The evaporator condensate can also become part of the alcohol/water solvent used in a continuous organosolv pulping process such as described in U.S. Patent Application Serial No. 07/649,683 or to precipitate the lignin in such a process. In yet another alternative, the bleaching filtrates can be concentrated and the concentrated material can be burned with recovery of energy. Material such as caustic can also be recovered.

As shown in Figure 6, pulp brownstock can be delignified and bleached in a continuous mode. The pulp brownstock in any given treatment stage can be washed in a countercurrent fashion with the bleaching filtrates obtained from washing the pulp at a subsequent treatment stage. Initially, pulp brownstock of a consistency of from about 10% to about 15% pulp solids is pumped through line 20. The pulp is mixed at

mixer 21 with a peroxy compound for example using peracetic acid (PA) or hydrogen peroxide (P) at a pH of from about 1.5 to 11 and in an amount of about 0.2% to 2% (w/w) peroxy compound on oven dried (o.d.) pulp.

- When hydrogen peroxide is used, it is introduced at liquid stream 76 into the reaction mixture in mixer 21. The final pH is preferably from about 8.5 to about 11 which can be maintained by addition of caustic such as sodium or potassium hydroxide to the reaction mixture into liquid stream 76. The pulp can be of any consistency, but is preferably between about 10 to about 12% by weight of pulp solids. When peracetic acid (PA) is used as a peroxy compound, the final pH is preferably from about 2 to about 5.

- When commercially available peracetic acid is used, it can be introduced at liquid stream 76. Peracetic acid can also be obtained by recovering and converting the acetic acid which is present in the evaporator condensate 70 from the solvent recovery tower used to recover the solvent in an organosolv pulping process such as is described in U.S. Patent No. 4,764,596 and Application Serial No. 07/649,683. The evaporator condensate 70 is pumped into process equipment 71 which generally includes conventional recovery equipment such as membrane concentration and solvent extraction equipment which can be used in a suitable combination with distillation, freeze concentration and the like. In process equipment 71, the acetic acid present in condensate 70 is recovered preferably to a 100% purity and a bottom stream 72 is also recovered as an aqueous solution which may be recycled for use with the water introduced at 61 at washer 6. After recovery of the acetic acid at process equipment 71, the acetic acid is pumped into process equipment 73. Process equipment 73 generally includes a conversion reactor wherein the acetic acid is converted in part to peracetic acid. In process equipment 73, hydrogen peroxide is introduced at liquid stream 82 and mixed with acetic acid in an appropriate ratio which can be carefully selected to optimize the conversion of acetic acid to peracetic acid at given process parameters. Sulfuric acid can be added at liquid stream 82 to the reaction mixture in process equipment 73 and the reaction is allowed to proceed at the appropriate process conditions to optimize the conversion of acetic acid to peracetic acid. Alternatively, commercially available acetic acid can be introduced at liquid stream 82 and converted in process equipment 73 to peracetic acid.

- After mixing with a peroxy compound, the pulp is pumped through line 22 into vessel 23 which can be selected from conventional bleaching equipment, such that the reaction time is preferably from about 0.3 to about 3 hours, the reaction temperature is between about 40°C and about 90°C, preferably 50°C to 70°C which can be maintained by using conventional heating techniques, such as steam injection.

- After peroxy compound treatment, the peroxy treated pulp is pumped through line 25 and washed in washer 3 using bleaching filtrates pumped through line 44 from subsequent treatment stages. After washing the pulp at washer 3, bleaching filtrates are removed through line 34 and can be recycled as described above. Washer 3 and washers 4, 5, and 6 can be selected from conventional washing equipment such as drum, belt, compaction baffle or pressure diffusion washers. Depending on the equipment selected, the pulp can be washed at atmospheric pressure and the water removed either by vacuum applied suction, by mechanical suction or by pressure concentric rings. The duration of the pulp washing at washer 3 and subsequent washers 4, 5 and 6 also depends on the equipment selected. After washing at washer 3, the pulp is pumped through line 30 into mixer 31 which is preferably a high shear mixer and can withstand the operating pressure required by the process. The pulp is at about 9 to about 40% consistency by weight of pulp solids. The pulp in mixer 31 is mixed with a caustic solution, for example a sodium hydroxide solution which is introduced at liquid stream 80. The amount of caustic added is preferably between from about 2% to about 8%, more preferably from about 3% to about 6%, (w/w) caustic on oven dry (o.d.) pulp. The pulp slurry thus obtained is further mixed at high shear with oxygen gas which is introduced at line 30 through liquid stream 79. The temperature of the reaction mixture in mixer 31 is preferably between from about 60°C and about 110°C, more preferably from about 70°C to about 90°C which can be achieved by steam injection. Oxygen pressure in mixer 31 is preferably maintained between about 30 and about 100 psig, more preferably between about 80 to about 100 psig. Additional chemical agents which can be added into liquid stream 79 to help preserve pulp strength properties include from about 0.1% to about 1% magnesium sulfate, from about 0.1% to about 1% diethylene triamine pentaacetic acid (DTPA), and from about 0.5% to up to about 3% sodium silicate. The pulp is pumped through line 32 into vessel 33 which can be selected from conventional bleaching equipment, but generally, vessel 33 is a pressurized vessel and is selected to achieve the required reaction time and temperature. The temperature of the reaction mixture in vessel 33 is preferably between from about 60°C and about 110°C, more preferably from about 70°C to about 90°C and heating of the reaction mixture in vessel 33 can be achieved if needed by steam injection. Oxygen pressure in vessel 33 is preferably maintained between about 30 and about 100 psig, more preferably between about 80 to about 100 psig and the reaction time is preferably between about 6 to about 60 minutes, more preferably between about 25 to about 50 minutes.

After oxygen delignification, the pulp is pumped through line 35 into washer 4 and is washed using countercurrent bleaching filtrates from line 54. After washing in washer 4, the delignified pulp is pumped through line 40 into equipment 41. Equipment 41 can be a mixer when the pulp is treated with a peroxy compound or can be a dewatering press when a high consistency pulp is treated with ozone. The pulp is
 5 mixed at mixer 41 with a peroxy compound for example using peracetic acid (PA) or hydrogen peroxide (P) at a pH of from about 3 to about 11 and in an amount of about 0.2 to about 2% (w/w) peroxy compound on oven dried (o.d.) pulp. When hydrogen peroxide is used, it is introduced at liquid stream 77 into the reaction mixture at mixer 41. The final pH is preferably from about 8.5 to about 11 which can be maintained by addition of caustic such as sodium or potassium hydroxide into liquid stream 77. The pulp can be of any
 10 consistency, but is preferably between about 10% to about 12% by weight of pulp solids. When peracetic acid (PA) is used as a peroxy compound, the final pH is preferably from about 2 to about 7 and the peracetic acid can be introduced either at liquid stream 77 or through line 75 from the acetic acid recovery and conversion at process equipment 71 and 73. After mixing with a peroxy compound, the pulp is pumped through line 42 into vessel 43 which can be selected from conventional bleaching equipment. Generally,
 15 vessel 43 is selected such that the reaction time in vessel 43 is from about 0.3 to about 3 hours, the reaction temperature is between about 40°C and 90°C, preferably 50°C to 70°C which can be maintained using conventional heating techniques, such as steam injection.

Alternatively, an ozone stage can also be used to treat pulp brownstock in vessel 43. Pulp treatment with ozone is carried at a pH of from about 1.5 to about 5, preferably from about 2 to about 3 and at a
 20 temperature of from about 20°C to about 60°C, preferably 25°C to 30°C. Two alternative methods of ozone bleaching can be used. In one method, with a high consistency pulp of from about 20% to 50%, the pulp is dewatered at equipment 41 which is preferably a high consistency pulp dewatering press. After dewatering, the pulp is conveyed through line 42 and into vessel 43 which can be selected from conventional bleaching equipment but which is preferably a high consistency ozone bleaching tower. In vessel 43, the pulp is
 25 fluffed using techniques known in the art and ozone gas is introduced into vessel 43 through line 46 and rapidly reacted with the pulp fibers at a concentration of from about 0.2% to about 2% (w/w) ozone on oven dried (o.d.) pulp. Alternatively, when a medium consistency pulp is used, ozone is introduced to the pulp as ozone solution or as ozone gas at mixer 41 which is preferably a high pressure mixer. Ozone solution is obtained from first pressurizing ozone gas over water at an elevated pressure sufficient to dissolve enough
 30 ozone in water such that the concentration of ozone is from about 0.2% to about 2% (w/w) ozone on oven dried (o.d.) pulp after the ozone solution is mixed with the pulp. The ozone solution is introduced into mixer 41 through liquid stream 77 and mixed with the pulp. The resulting reaction mixture is pumped through line 42 into vessel 43 which is a conventional bleaching tower preferably selected to conform to the reaction parameters. The final pH can be adjusted to the appropriate level using an acid such as sulfuric acid which
 35 can be introduced at liquid stream 77 into mixer 41. The pulp is then pumped through line 45 onto washer 5 and, if need be, the pulp pH can be adjusted using caustic at liquid stream 47 to a pH of from about 9 to 11 and can be further adjusted to a near neutral pH by successive washing with countercurrent filtrates from line 64.

After a first peroxy compound treatment stage or an ozone treatment stage, the pulp is pumped through
 40 line 45 onto washer 5 and is washed using countercurrent bleaching filtrates from line 64. After washing in washer 5, the pulp is pumped through line 50 into mixer 51. The pulp is mixed at mixer 51 with a peroxy compound for example using peracetic acid (PA) or hydrogen peroxide (P) at a pH of from about 3 to about 11 and in an amount of about 0.2% to about 2% (w/w) peroxy compound on oven dried (o.d.) pulp. When
 45 hydrogen peroxide is used, it is introduced at liquid stream 81 into the reaction mixture at mixer 51. The final pH is preferably from about 8.5 to 11 about which can be maintained by addition of caustic such as sodium or potassium hydroxide into liquid stream 81. The pulp can be of any consistency, but is preferably between about 10% to about 12% by weight of pulp solids. When peracetic acid (PA) is used as a peroxy compound, the final pH is preferably from about 2 to about 7 and the peracetic acid can be introduced either at liquid stream 81 or through line 78 from the acetic acid recovery and conversion at process
 50 equipment 71 and 73. After mixing with a peroxy compound, the pulp is pumped through line 52 into vessel 53 which can be selected from conventional bleaching equipment, such that the reaction time is preferably from about 0.3 to about 3 hours, the reaction temperature is between about 40°C and about 90°C, preferably 50°C to about 60°C which can be maintained by using conventional heating techniques, such as steam injection. The delignified and bleached pulp is removed at line 62 and can be suitably subjected to
 55 further processing or drying.

Alternatively, as shown in Figure 7, pulp brownstock 10 of a consistency of from about 9% to about 40% pulp solids is pumped through line 120 into mixer 121 which is preferably a high shear mixer and can withstand the operating pressure required for the process. The pulp in mixer 121 is mixed with a caustic

solution, for example a sodium hydroxide solution which is introduced in liquid stream 176. The amount of caustic added is preferably between from about 2% to about 8%, more preferably from about 3% to about 6% (w/w) caustic on oven dry (o.d.) pulp. The pulp slurry thus obtained is further mixed at high shear with oxygen gas which is introduced at line 120 through line 179. The temperature of the reaction mixture in mixer 121 is preferably between from about 60°C and about 110°C, more preferably from about 70°C to about 90°C which can be achieved by steam injection. Oxygen pressure in mixer 121 is preferably maintained between about 30 and about 100 psig, more preferably between about 80 to about 100 psig. Additional chemical agents which may be added into liquid stream 176 to help preserve pulp strength properties include from about 0.1% to about 1% magnesium sulfate, from about 0.1% to about 1% diethylene triamine pentaacetic acid (DTPA), and from about 0.5% to up to about 3% sodium silicate. The pulp is pumped through line 122 into vessel 123 which can be selected from conventional bleaching equipment, but generally, vessel 123 is a pressurized vessel and is selected to achieve the required reaction time and temperature. The temperature of the reaction mixture in vessel 123 is preferably between from about 60°C and about 110°C, more preferably from about 70°C to about 90°C and heating of the reaction mixture can be achieved by steam injection. Oxygen pressure in vessel 123 is preferably maintained between about 30 and about 100 psig, more preferably between about 80 to about 100 psig and the reaction time is preferably between about 6 to about 60 minutes, more preferably between about 25 to about 50 minutes.

After oxygen delignification, the pulp is pumped through line 125 into washer 13 and is washed using water introduced at 160. Washer 13 and washers 14, 15, and 16 can be selected from conventional washing equipment such as drum, belt, compaction baffle washer or pressure diffusion washers. Depending on the equipment selected, the pulp can be washed at atmospheric pressure and the water removed either by vacuum applied suction, by mechanical suction or by pressure concentric rings. The duration of the pulp washing at washer 13 and washers 14, 15 and 16 also depends on the equipment selected. After washing the pulp at washer 13, bleaching filtrates are removed through line 134 and can be recycled as described above.

After washing in washer 13, the delignified pulp is pumped through line 130 into mixer 131. The delignified pulp in mixer 131 is mixed with a liquid solution of chlorine dioxide introduced at liquid stream 180 and containing chlorine dioxide in the range of from about 0.1% to about 2% (w/w) chlorine dioxide on oven dry (o.d.) pulp. The temperature of the reaction mixture in mixer 131 is from about 30°C to about 70°C which can be achieved by steam injection. The reaction mixture is pumped through line 132 into vessel 133 which can be selected from conventional bleaching equipment, but generally, vessel 133 is selected to achieve the required reaction time and temperature. The reaction in vessel 133 proceeds at a temperature of from about 30 to about 70°C and the reaction time is of about 0.3 to about 3 hours, preferably 0.3 to 2 hour. The chlorine dioxide bleaching reaction in vessel 133 is carried forward at a final pH of from about 2 to about 3 and caustic or acid may be added at liquid stream 180 as need be to maintain the pH in this range. The chlorine dioxide bleached pulp is pumped through line 135 and washed on washer 14 using countercurrent washing with bleaching filtrates from washer 15 pumped through line 154. Filtrates resulting from washing the pulp at washer 14 are pumped through line 140 and subjected to conventional treatment to remove any chlorine and chlorinated products. After treatment, the resulting bleaching filtrates can be combined with bleaching filtrates from line 134 and can be recycled as described above.

After washing at washer 14, the washed pulp at a consistency of about 9 to about 15%, preferably from about 11 to about 12% by weight of pulp solids is pumped through line 142 and into mixer 141 which is preferably a high shear mixer and can withstand the operating pressure required by the process. The pulp slurry in mixer 141 is mixed with a caustic solution introduced at liquid stream 177 and containing of from about 2% to about 5%, preferably from about 2.5% to about 4% (w/w) sodium hydroxide on oven dry (o.d.) pulp. The pulp slurry thus obtained is further mixed at high shear with oxygen gas which is introduced at line 140 through line 182. The temperature of the reaction mixture in mixer 141 is preferably between about 60°C and about 110°C, more preferably between about 70°C and about 90°C which can be achieved by steam injection. Oxygen pressure in mixer 141 is preferably maintained between about 30 to about 100 psig, preferably at about 30 to about 60 psig. Additional chemical agents may be added into liquid stream 177 such as magnesium sulfate from about 0.1% to about 1%. The pulp is pumped into vessel 143 which can be selected from conventional bleaching equipment, but generally vessel 143 is selected to achieve the required reaction time and temperature. The temperature of the reaction mixture in vessel 143 is preferably between about 60°C and about 110°C, more preferably between about 70°C and about 90°C which can be achieved by steam injection and the total reaction time with oxygen in vessel 143 is preferably between about 6 and about 60 minutes. Oxygen pressure in vessel 143 is decreased to atmospheric pressure during the first 10 to 15 minutes and the pulp remains in vessel 143 in an oxygen rich atmosphere for about 20 to

about 40 minutes.

Alternatively, after washing at washer 14, in an alkaline extraction stage, the pulp slurry in mixer 141 can be mixed with a caustic solution introduced at liquid stream 177 and containing of from about 0.5% to about 2% (w/w) caustic on oven dry (o.d.) pulp. The temperature of the reaction mixture in mixer 141 is preferably between about 40°C and about 70°C which can be achieved by steam injection. Additional chemical agents may be added into liquid stream 177 such as magnesium sulfate from about 0.1% to about 1%. The pulp is pumped into vessel 143 which can be selected from conventional bleaching equipment, but generally vessel 143 is selected to achieve the required reaction time and temperature. The temperature of the reaction mixture in vessel 143 is preferably between about 40°C and about 70°C which can be achieved by steam injection and the total reaction time with oxygen in vessel 143 is from about 1.5 to about 3 hours, preferably 1.5 to 2 hours.

After the oxidative extraction stage or the alkaline extraction stage, the pulp is pumped through line 145 into washer 15. The pulp is washed in washer 15 using bleaching filtrates pumped through line 164 and obtained by washing the pulp at washer 16. The bleaching filtrates obtained at washer 15 are pumped through line 154 and used to wash the pulp in washer 14. After washing the pulp on washer 15, the delignified pulp is pumped through line 150 into mixer 151. The delignified pulp in mixer 151 is mixed with a liquid solution of chlorine dioxide introduced at liquid stream 181 and containing chlorine dioxide in the range of from about 0.2% to about 2% (w/w) chlorine dioxide on oven dry (o.d.) pulp. The temperature of the reaction mixture in mixer 151 is from about 30° to about 70°C which can be achieved by steam injection. The reaction mixture is pumped through line 152 into vessel 153 which can be selected from conventional bleaching equipment, but generally, vessel 153 is selected to achieve the required reaction time and temperature. The reaction in vessel 153 proceeds at a temperature of from about 30 to about 70°C and the reaction time is from about 0.3 to about 3 hours, preferably 1.5 to about 3 hours. The reaction in vessel 153 is carried forward at a final pH of from about 3.5 to about 4.5 and caustic may be added at liquid stream 181 to maintain the pH in this range. The chlorine dioxide bleached pulp in vessel 153 is pumped through line 155 and washed at washer 16 using water introduced at line 161. Bleaching filtrates are removed from washer 16 through line 164 and can be used to wash the pulp at washer 15. The delignified and bleached pulp is removed at line 162 and can be suitably subjected to further processing or drying.

Alternatively, as shown in Figure 8, pulp brownstock 10 of a consistency of from about 9% to about 40% pulp solids is pumped through line 220 into mixer 221 which is preferably a high shear mixer and can withstand the operating pressure required for the process. The pulp in mixer 221 is mixed with a caustic solution, for example a sodium hydroxide solution which is introduced in liquid stream 276. The amount of caustic added is preferably between from about 2% to about 8%, more preferably from about 3% to about 6% (w/w) caustic on oven dry (o.d.) pulp. The pulp slurry thus obtained is further mixed at high shear with oxygen gas which is introduced at line 220 through line 279. The temperature of the reaction mixture in mixer 221 is preferably between from about 60°C and about 110°C, more preferably from about 70°C to about 90°C which can be achieved by steam injection. Oxygen pressure in mixer 221 is preferably maintained between about 30 and about 100 psig, more preferably between about 80 to about 100 psig. Additional chemical agents which may be added into liquid stream 276 to help preserve strength properties include 0.1% to about 1% magnesium sulfate, from about 0.1% to 1% diethylene triamine pentaacetic acid (DTPA), and from about 0.5% to up to about 3% sodium silicate. The pulp is pumped through line 222 into vessel 223 which can be selected from conventional bleaching equipment, but generally, vessel 223 is a pressurized vessel and is selected to achieve the required reaction time and temperature. The temperature of the reaction mixture in vessel 223 is preferably between from about 60°C and about 110°C, more preferably from about 70°C to about 90°C and heating of the reaction mixture can be achieved by steam injection. Oxygen pressure in vessel 223 is preferably maintained between about 30 and about 100 psig, more preferably between about 80 to about 100 psig and the reaction time is preferably between about 6 to about 60 minutes, more preferably between about 25 to about 50 minutes.

After oxygen delignification, the pulp is pumped through line 225 into washer 23 and is washed using countercurrent bleaching filtrates from line 244. Washer 23 and washers 24 and 25 can be selected from conventional washing equipment such as drum, belt, compaction baffle or pressure diffusion washers. The bleaching filtrates are removed from washer 23 through line 234 and can be recycled as described above.

After washing the pulp in washer 23, the delignified pulp is pumped through line 230 into equipment 231. Equipment 231 can be a mixer when the pulp is treated with a peroxy compound or can be a dewatering press when a high consistency pulp is treated with ozone. The pulp is mixed in mixer 231 with a peroxy compound for example using peracetic acid (PA) or hydrogen peroxide (P) at a pH of from about 3 to about 11 and in an amount of about 0.2% to about 2% (w/w) peroxy compound on oven dried (o.d.) pulp.

When hydrogen peroxide is used, it is introduced at liquid stream 280 into the reaction mixture at mixer 231. The final pH is preferably from about 8.5 to about 11 which can be maintained by addition of caustic such as sodium or potassium hydroxide into liquid stream 281. The pulp can be of any consistency, but is preferably between about 10% to 12% by weight of pulp solids. When peracetic acid (PA) is used as a peroxy compound, the final pH is preferably from about 2 to about 5 and the peracetic acid can be introduced either at liquid stream 280 or through line 275 from the acetic acid recovery and conversion through process equipment 71 and 73. After mixing with a peroxy compound, the pulp is pumped through line 232 into vessel 233 which can be selected from conventional bleaching equipment, such that the reaction time is from about 0.3 to about 3 hours, the reaction temperature is between about 40° C and about 90° C, preferably 50° to about 60° C which can be maintained by using conventional heating techniques, such as steam injection.

Alternatively, an ozone stage can also be used to treat pulp brownstock in vessel 233. Pulp treatment with ozone is carried at a pH of from about 1.5 to about 5, preferably from about 2 to about 3 and at a temperature of from about 20° to about 60° C, preferably 25° to 30° C. Two alternative methods of ozone bleaching can be used. In one method, for a high consistency pulp of from about 20% to about 50%, the pulp is dewatered at equipment 231 which is preferably a high consistency pulp dewatering press. After dewatering, the pulp is pumped through line 232 and into vessel 233 which can be selected from conventional bleaching equipment but is preferably a high consistency ozone bleaching tower.

At the top of vessel 233, the pulp is fluffed and ozone gas is introduced at line 236 into vessel 233 and rapidly reacted with the pulp fibers at a concentration of from about 0.2% to about 2% (w/w) ozone on oven dried (o.d.) pulp. Alternatively, when a medium consistency pulp is used, ozone is introduced to the pulp in mixer 231 as a solution or a gas. Ozone solution is obtained from first pressurizing the ozone over water at an elevated pressure sufficient to dissolve enough ozone such that the concentration of ozone is from about 0.2% to 2% (w/w) ozone on oven dried (o.d.) pulp after the ozone solution is mixed with the pulp. The ozone solution is introduced into mixer 231 through liquid stream 280 and mixed with the pulp. The resulting reaction mixture is pumped through line 232 into vessel 233 which is a conventional bleaching tower preferably selected to conform to the reaction parameters. The pH may be adjusted to the appropriate level using an acid such as sulfuric acid which can be introduced at liquid stream 281 and into mixer 231 through line 230. The pulp is then pumped through line 235 and into washer 24 and, if need be, the pulp pH can be adjusted using caustic to a pH of from about 9 to about 11 which can be introduced through liquid stream 237 and can be further adjusted to a neutral pH by successive washing with water which is introduced at line 263.

After the peroxy compound treatment stage or the ozone treatment stage, the pulp is pumped through line 235 into washer 24. The pulp is washed in washer 24 using water introduced at line 263. The bleaching filtrates obtained at washer 24 are pumped through line 244 and used to wash the pulp on washer 23. After washing of the pulp on washer 24, the pulp is pumped through line 240 into mixer 241. The pulp in mixer 241 is mixed with a liquid solution of chlorine dioxide introduced at liquid stream 277 and containing chlorine dioxide in the range of from about 0.1% to about 2% (w/w) chlorine dioxide on oven dry (o.d.) pulp. The temperature of the reaction mixture in mixer 241 is from about 30° to about 70° C which can be achieved by steam injection. The reaction mixture is pumped through line 242 into vessel 243 which can be selected from conventional bleaching equipment, but generally, vessel 243 is selected to achieve the required reaction time and temperature. The reaction in vessel 243 proceeds at a temperature of from about 30° to about 70° C and the reaction time is of about 0.3 to about 3 hours, preferably 1.5 to 3 hours. The reaction mixture in vessel 243 is carried forward at a final pH of from about 2 to about 4.5 and caustic may be added at liquid stream 277 as need be to maintain the pH in this range. The chlorine dioxide bleached pulp in vessel 243 is pumped through line 245 and washed at washer 25 using water introduced at line 261. Filtrates resulting from washing the pulp at washer 25 are pumped through line 254 and subjected to conventional treatment to remove any chlorine and chlorinated compounds. After treatment, the resulting bleaching filtrates can be combined with bleaching filtrates from line 234 and can be recycled as above. The delignified and bleached pulp is removed at line 262 and can be suitably subjected to further processing or drying.

Except where noted otherwise, in the following examples all pulps are organosolv pulps which are prepared using an organosolv pulping process. After pulping, the pulp is cooled, removed from the extraction vessel and further screened as is customary in pulping practice to result in a pulp brownstock having the kappa numbers and viscosities indicated in each example.

It is believed that the enhanced novel effects proven with organosolv pulps are applicable to pulps in general. Therefore, the following examples should not be construed to limit the present invention to any particular pulp.

The following two examples show the effect of oxygen delignification of an organosolv pulp.

Example 1

5 Sequence O

Birch/maple/aspen organosolv pulp was mixed with 4% sodium hydroxide and 0.5% MgSO_4 at a consistency of 12% and placed in the mixing chamber of a Quantum Technologies Mark II high shear mixer. The chamber was then capped and flushed with O_2 gas by bringing it to pressure with O_2 and releasing, then filling the chamber to the final O_2 pressure of 100 psig. The pulp was then mixed at high speed for 4 seconds at this pressure, and was reacted for 45 minutes at 85°C, with occasional stirring at low speed.

The results are shown below.

15

	Kappa No.	Viscosity (cps)
1. Organosolv brownstock	36.1	23.8
2. Oxygen delignification	8.1	22.4

20

As can be readily seen, the kappa number of the delignified pulp was reduced by about 63%, while the viscosity remained virtually the same.

Example 2

25

Sequence O

Aspen organosolv pulp was treated as in Example 1, except that the oxygen pressure was maintained at 80 psig.

30

	Kappa No.	Viscosity (cps)
1. Organosolv brownstock	36.6	20.7
2. Oxygen delignification	9.0	18.9

35

The decrease in kappa number was about 75%, with a small decrease in viscosity of about 2 cps. In both Examples 1 and Example 2, the decrease in kappa number was approximately 70% to a final kappa number in the range of 9 to 13 with a small decrease in viscosity on the order of about 2 cps or less.

40 Example 3

Kraft softwood brownstock obtained from Skeena Cellulose Incorporated, Prince Rupert, British Columbia was treated as in Example 1. As shown in Figure 2 by closed circles, the viscosity of the organosolv pulp was essentially unchanged with increased oxygen delignification. By contrast, the Kraft brownstock pulp, shown by open circles in Figure 2, shows a linear viscosity decrease with increasing oxygen delignification.

In Examples 4 and 5 an oxidative extraction (E_o) process was used to delignify organosolv pulp as a first stage.

50 Example 4

Sequence E_o

Aspen organosolv pulp was placed in the mixing chamber of a Quantum Technologies Mark II high shear mixer. A charge of 4% sodium hydroxide and 0.5% MgSO_4 was injected into the sealed chamber at about 11% to 12% consistency. Oxygen was mixed with the pulp at 32 psig in the high shear mixer for four seconds. Over the next 12 minutes oxygen pressure was gradually released until pressure was atmospheric. The pulp remained in the mixer at 70°C for another 45 minutes, with occasional stirring at low

speed.

	Kappa No.	Viscosity (cps)
1. Organosolv brownstock	32.2	29.8
2. Oxygen extraction (E_o)	16.7	26.7

Example 5

Sequence E_o

Birch/maple/aspen organosolv pulp was treated as in Example 4, except that the initial oxygen pressure was 60 psig.

	Kappa No.	Viscosity (cps)
1. Organosolv brownstock	36.7	17.6
2. Oxygen extraction (E_o)	18.2	17.8

Examples 4 and 5 demonstrate that when oxidative extraction conditions are used, the kappa number of the pulp is decreased by about 50% to a final kappa number in the range of 16 to 18 with a slight decrease in viscosity on the order of about 3 cps or less. An advantage to using oxidative extraction is that it requires lower capital investment from the standpoint of bleach plant construction or design.

In the following example pulp is first delignified with oxygen and then treated with peracetic acid.

Example 6

Sequence O(PA)

Birch/maple/aspen organosolv pulp was delignified with oxygen as in Example 1 to a kappa number of 10.3 and was subsequently treated with peracetic acid. The oxygen delignification was carried out by mixing a pulp slurry at about 12% consistency with a 4% solution of NaOH at 85°C, 100 psig for 45 minutes. 1.0% $MgSO_4$ was also added to the reaction mixture.

The peracetic acid stage was carried by mixing either 2.7% or 1.3% peracetic acid and 2.5% NaOH or 4.0% NaOH respectively at a 10% consistency. Additionally, 0.5% DTPA, 0.5% $MgSO_4$, and 4.0% Na_2SiO_4 were added to both of the respective reaction mixtures. The reaction time was 1 hour at 60°C.

The results of such treatments are shown below:

	Kappa No.	Viscosity (cps)	Brightness (ISO)
1. Organosolv brownstock	29.0	22.9	—
2. Oxygen delignification	10.3	22.5	36.4
3. Oxygen delignification + 1.3% peracetic acid	5.3	24.1	58.5
4. Oxygen delignification + 2.7% peracetic acid	4.0	22.3	64.7

The foregoing shows that an oxygen delignification of about 65% is significantly increased by approximately another 50% to a kappa number of about 5.3 to 4, with virtually no decrease in viscosity, when oxygen delignification of pulp is followed by a peracetic acid treatment stage. Such a treatment step also significantly increases the brightness of the pulp from about 37 ISO to about 59 to 65 ISO.

In the following example, pulp delignified with oxygen was treated with two stages of exposures to peroxy compounds after oxygen delignification.

Example 7

Sequence O(PA)(PA) and O(PA)P

The oxygen delignified pulp of Example 6 was subsequently treated with either a 1.3% or 2.7% peracetic acid treatment stage as described in Example 6. A third treatment stage was then performed with either 1.3% peracetic acid or 1.0% hydrogen peroxide. The peracetic acid third treatment stage was carried out by reacting 1.3% peracetic acid, 2.5% NaOH, 0.1% MgSO₄, 0.1% DTPA, and 2.0% Na₂SiO₄ for one hour at 60°C at a 10% consistency. The hydrogen peroxide third treatment stage was carried out by reacting the pulp with 1.0% H₂O₂, 1.0% NaOH, 0.2% MgSO₄, 0.2% DTPA, and 4.0% Na₂SiO₄ at 60°C and a 10% consistency for one hour. The hydrogen peroxide fourth stage treatment was accomplished by reacting the pulp with 1% H₂O₂, 0.8% NaOH, and 0.5% DTPA at a 12% consistency for 60 minutes at 70°C.

The results of these treatments are shown below:

	<u>Kappa No.</u>	<u>Viscosity (cps)</u>	<u>Brightness (ISO)</u>
1. Organosolv Brownstock	29.0	22.9	—
2. Oxygen delignification	10.3	22.5	36.4
3. Oxygen delignification + 1.3% peracetic acid + 1.3% peracetic acid	— *	17.5	68.1
4. Oxygen delignification + 2.7% peracetic acid + 1.3% peracetic acid	— *	21.7	76.5
5. Oxygen delignification + 2.7% peracetic acid + 1.0% hydrogen peroxide	— *	14.8	76.5

* The kappa numbers were too low to be accurately measured.

The successive stages of peracetic acid treatment following oxygen delignification in runs 3 and 4 resulted in high brightness levels of 68.1 ISO and 76.5 ISO, again with only a small decrease in viscosity (5 and 1 cps respectively). Treatment with hydrogen peroxide in run 5 appears to cause a significantly larger decrease in viscosity, although the brightness level is also 76.5 ISO.

It should be noted that the above-described brightness levels were achieved without any chlorine containing bleaching compounds and therefore the delignified and bleached pulp contain zero level TOX from chlorine based bleaching chemicals and correspondingly the bleaching effluent contain zero level of AOX.

Example 8

Sequence O(PA)D and O(PA)DD

The organosolv pulp from Example 5 was delignified with oxygen to a kappa number of 10.3 as in Example 6. The pulp was then bleached using successive treatment stages of peracetic acid and chlorine dioxide. The delignification and peracetic acid second stage treatments were carried out as in Example 7. The 0.4% and 0.8% chlorine dioxide third treatment stages were accomplished respectively by reacting either 0.4% ClO₂ and no NaOH with the pulp at a 10% consistency for 3 hours at 70°C, or by reacting 0.8% ClO₂ and 0.35% NaOH with the pulp under the same conditions. The fourth treatment stage with 0.4% chlorine dioxide was carried out by reacting 0.4% ClO₂ and 0.1% NaOH at a 10% consistency for 3 hours at 70°C.

The results of such treatments are shown below.

	<u>Kappa No.</u>	<u>Viscosity (cps)</u>	<u>Brightness (ISO)</u>
5	1. Oxygen delignification	10.3	22.5
			36.4
	2. Oxygen delignification + 2.7% peracetic acid	4.0	22.3
			64.7
10			
	3. Oxygen delignification + 2.7% peracetic acid + 0.4% chlorine dioxide	_____ *	21.9
15			75.9
	4. Oxygen delignification + 2.7% peracetic acid + 0.8% chlorine dioxide	_____ *	20.8
20			86.3
	5. Oxygen delignification + 2.7% peracetic acid + 0.4% chlorine dioxide + 0.4% chlorine dioxide	_____ *	19.8
25			89.6

* The kappa numbers were too low to be accurately measured.

30 While in all cases the pulp brightness was significantly enhanced by the successive treatment stages with peracetic acid and chlorine dioxide with little decrease in viscosity (3 cps or less), the treatments that included the chlorine dioxide treatment stage yielded significant increases in brightness, to levels above 80 ISO. In particular, the difference between treatment runs 4 and 5, namely the splitting up of the chlorine dioxide treatment stage by the usual washing step raised the brightness level by a significant 3 points. The quantities of chlorine dioxide required to achieve a brightness above 89 ISO is low enough that bleach plant effluents would contain below 0.5 kg AOX per ton of pulp in the untreated effluent.

35 In the following example a hydrogen peroxide treatment stage preceded delignification with oxygen. Some of the delignification stages were followed by various peroxy treatment stages.

40 Example 9

Sequence PO, POP, PO(PA) and PO(PA)P

45 Birch/maple/poplar organosolv pulp was treated with hydrogen peroxide prior to oxygen delignification of the pulp. The pretreatment or first stage treatment was carried out with 2.0% H₂O₂, 2.8% NaOH, 0.5% DTPA, and 0.5% MgSO₄ at a 12% consistency at 70°C for one hour. The oxygen delignification second stage was carried out with 4.0% NaOH, 0.5% MgSO₄ at a 12% consistency at 85°C for 45 minutes. The third stage hydrogen peroxide was accomplished by reacting treated pulp with 2% H₂O₂, 1% NaOH, 0.5% MgSO₄, and 0.5% DTPA at 70°C for 45 minutes. The third stage peracetic acid stage was accomplished by reacting 1.5% peracetic acid, 1.5% NaOH, 0.5% DTPA, and 0.5% MgSO₄ at a 12% consistency at 70°C for 3 hours. The fourth stage hydrogen peroxide stage was carried out by reacting 1% H₂O₂, 0.8% NaOH, and 0.5% DTPA at a 12% consistency for 60 minutes at 70°C.

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		<u>Kappa No.</u>	<u>Viscosity (cps)</u>	<u>Brightness (ISO)</u>
5	1. Organosolv brownstock	36.4	22.6	25.7
	2. 2.0% Hydrogen peroxide + Oxygen delignification	6.1	19.4	51.4
10	3. 2.0% Hydrogen peroxide + Oxygen delignification + 2.0% hydrogen peroxide	3.0	15.1	66.4
15	4. 2.0% Hydrogen peroxide + Oxygen delignification + 1.5% peracetic acid	2.3	20.1	72.3
20	5. 2.0% Hydrogen peroxide + Oxygen delignification + 1.5% peracetic acid + 1.0% hydrogen peroxide	_____*	14.8	83.0

* The kappa numbers were too low to be accurately measured.

In all cases, pretreatment of pulp with hydrogen peroxide prior to delignification with oxygen followed by a peroxy treatment yielded pulps with kappa numbers greatly reduced (83% or more), a small loss of viscosity (8 cps or less), and brightness levels in the range of 66.4 ISO to 83 ISO. In particular, a brightness level of 83 without use of any chlorine compounds while retaining a viscosity above 14, was obtained. Figure 5 is a beating curve for the organosolv pulp of this example delignified and bleached with the sequence PO(PA)P. With the PO(PA)P sequence, a brightness of 83 ISO can be obtained without significant loss of pulp strength. Such organosolv is bleached to 83 ISO without chlorine dioxide and contain zero level TOX from chlorine based bleaching chemicals and correspondingly the bleach effluents contain zero level AOX.

In the following example, the effect of pretreatment with peracetic acid or a soured peracetic acid treatment stage is shown.

Example 10

Sequence (PA)O, (PA)O(PA), (soured PA)O, (soured PA)O(PA), (soured PA)OP and (soured PA)ODED

Birch/maple/poplar organosolv brownstock was either bleached using 2% peracetic acid or first soured using an H₂SO₃ wash and then treated with the 2% peracetic acid before the pulp was oxygen delignified. The pulp was further bleached using chlorine dioxide, peroxide and/or peracetic acid.

The 2% peracetic acid first treatment stage was carried out by reacting the pulp with 2% peracetic acid, 0.5% DTPA, and 0.5% MgSO₄ at a 12% consistency for 2 hours at 70 °C. The 2% peracetic acid third treatment stage was carried out by reacting the pulp with 2% peracetic acid, 0.5% DTPA, 0.5% MgSO₄ at a 12% consistency for 2 hours at 70 °C and at alkaline pH adjusted to a pH of 5 to 7 by addition of caustic. The soured peracetic wash was accomplished by washing the pulp with water through which SO₂ gas was bubbled to a pH of 2 to 3. The oxygen delignification was carried out with 4% NaOH and 0.5% MgSO₄ at a 12% consistency at 100 psig and 85 °C for 45 minutes. The third stage chlorine dioxide treatment for run 5 was carried out by reacting the pulp with 0.5% ClO₂ for 2 hours at 70 °C. This was followed by a sodium hydroxide extraction fourth stage, as is customary practice in bleaching technology, in which the pulp was extracted with 2% NaOH at a 12% consistency for 2 hours at 70 °C. For the fifth stage the pulp was reacted with 0.6% ClO₂, 0.22% NaOH at a 12% consistency for 3 hours at 70 °C. The third stage hydrogen

peroxide treatment stage for run 6 was carried out by reacting 2.2% NaOH, 0.5% DTPA, and 1.0% Na₂SiO₄ at 15% consistency for 2 hours at 70°C. For run 7, the third stage 1% hydrogen peroxide treatment was carried out by reacting the pulp with 1% H₂O₂, 1% NaOH, 1% NaSiO₄, 0.5% DTPA at 70°C for 1 hour.

The results are shown below:

5

		<u>Kappa No.</u>	<u>Viscosity (cps)</u>	<u>Brightness (ISO)</u>
10	1. Organosolv brownstock	36.3	15.0	—
	2. 2.0% peracetic acid + Oxygen delignification	5.6	13.6	50.6
15	3. 2.0% peracetic acid + Oxygen delignification + 2.0% peracetic acid	— *	13.3	73.6
20	4. H ₂ SO ₃ wash + 2.0% peracetic acid + Oxygen delignification	5.0	12.4	53.8
25	5. H ₂ SO ₃ wash + 2.0% peracetic acid + Oxygen delignification + 0.5% chlorine dioxide + 2.0% alkaline extraction + 0.6% chlorine dioxide	— *	10.9	89.8
30	6. H ₂ SO ₃ wash + 2.0% peracetic acid + Oxygen delignification + 1.0% peracetic acid	— *	12.7	72.2
35	7. H ₂ SO ₃ wash + 2.0% peracetic acid + Oxygen delignification + 1.0% hydrogen peroxide	— *	10.0	72.0

* The kappa numbers were too low to be accurately measured.

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It is seen that in all cases the kappa numbers were decreased well below 70%, viscosity decreases were on the order of 2 to 5 cps, and brightness levels achieved ranged from about 50 to above 89 ISO.

45 Example 11

Sequence (PA)O

In this example, a comparison is made between generated peracetic acid and commercially available peracetic acid. Birch/poplar/maple organosolv brownstock was treated according to Example 10 first with 1.1% peracetic acid then was oxygen delignified.

The results are shown below:

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	Kappa No.	Viscosity (cps)	Brightness (ISO)
1. Organosolv Brownstock	29.7	25.3	—
2. Gen. Peracetic Acid + Oxygen Delignification	5.5	24.8	53.2
3. Com. Peracetic Acid + Oxygen Delignification	5.7	22.7	51.6

In this example, pulp can be treated with either generated or commercially available peracetic acid. One of the techniques which can be used to generate peracetic acid is by conversion of acetic acid in the presence of hydrogen peroxide under acidic conditions. Hydrogen peroxide and acetic acid are mixed in an appropriate ratio selected to optimize the conversion to peracetic acid at given process parameters.

This example shows that under the same reaction conditions, similar brightening responses are obtained using either generated or commercial peracetic acid.

Examples 12 and 13 demonstrate the lower levels of oxygen delignification achieved with kraft pulps even when they are pretreated with peracetic acid. Additionally, there are greater losses of viscosity, and lower brightness levels when compared to the similarly treated pulps according to the methods of the present invention.

Example 12

Sequence (PA)O

Kraft softwood brownstock obtained from Skeena Cellulose Incorporated, Prince Rupert, British Columbia was delignified with oxygen by reacting the brownstock with 3.0% NaOH at 80 °C for 30 minutes. The brownstock was pretreated prior to delignification by reacting the pulp with 1.0% peracetic acid, 2.2% NaOH, 0.5% DTPA, and 0.5% MgSO₄ at a pH of 11 for two hours at 70 °C.

	Kappa No.	Viscosity (cps)	Brightness (ISO)
1. Kraft Brownstock	33.2	44.2	—
2. Oxygen delignification	21.1	28.8	25.6
3. 1.0% peracetic acid + Oxygen delignification	19.0	23.3	34.5

Clearly the reduction in the kappa number was much less, 36% and 42%, than for similarly treated organosolv pulps. At the same time, the loss in viscosity was significant (21 to 14 cps), while the brightness levels achieved fell short of the values achieved for similarly treated organosolv pulps.

In the following example the effect of additional peracetic acid bleaching of kraft softwood brownstock is shown.

Example 13

Sequence (PA)O(PA)

The kraft softwood brownstock of Example 10 was pretreated with peracetic acid and subsequently delignified with oxygen. After delignification with oxygen, the pulp was treated with peracetic acid as per Example 10.

	Kappa No.	Viscosity (cps)	Brightness (ISO)
1. Kraft brownstock	33.2	44.2	22.8
2. 2.0% peracetic acid + Oxygen delignification	16.8	17.3	29.2
4. 2.0% peracetic acid + Oxygen delignification + 1.4% peracetic acid	9.4*	17.6	44.9

* A 25 ml permanganate number can be used as an indication of lignin content when the kappa number is low. As a rough estimate, the kappa number is approximately 1.5 times the permanganate number.

The viscosity decreases were much larger than with similarly treated organosolv pulps and the brightness levels were not as high.

In another aspect of this invention, oxygen delignified organosolv pulps can be bleached to high brightness levels using two chlorine dioxide bleaching (D) stages with an alkaline extraction (E) stage
5 between them (ODED bleaching sequence).

Example 14

Sequence ODED

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Organosolv pulp was delignified with oxygen to a kappa number of 9.7 using the conditions of Example 1. This pulp was further contacted with 0.97% ClO_2 at a pulp consistency of 10% solids for 2 hours at 70 °C. After washing, the pulp was contacted with 2.0% NaOH at 12% consistency for 2 hours at 70 °C. This pulp was then washed and contacted with 0.8% ClO_2 , and enough NaOH to reach a pH of 3.5 to 4.5
15 for 3 hours at 70 °C.

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	Kappa No.	Viscosity (cps)	Brightness (ISO)
1. Organosolv brownstock	35	24.3	—
2. Oxygen delignification	9.7	20.1	—
3. Oxygen Delignification + 1st ClO ₂ Stage + Alkaline Extraction + 2nd ClO ₂ Stage	—	15.9	91

As can be readily seen, the kappa number of the pulp was reduced by about 62% by oxygen delignification and a final brightness of 91 ISO was achieved.

5 Example 15

Sequence ODED

10 Organosolv pulp was delignified with oxygen to a kappa number of 12.9 using the conditions of Example 1. This pulp was further contacted with 1.42% ClO_2 at a pulp consistency of 10% solids for 2 hours at 70 °C. After washing, the pulp was contacted with 2.0% NaOH at 12% consistency for 2 hours at 70 °C. This pulp was then washed and contacted with 0.7% ClO_2 and 0.3% NaOH for 3 hours at 70 °C.

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	Kappa No.	Viscosity (cps)	Brightness (ISO)
1. Brownstock	37.4	17.6	—
2. Oxygen delignification	12.9	16.1	—
3. Oxygen Delignification + 1st ClO ₂ Stage + Alkaline Extraction + 2nd ClO ₂ Stage	—	11.0	90.2

The pulp of this example was analyzed for residual chloroorganic content and found to have the following levels:

Total TOX	158.0 ppm
Water leachable AOX	5.4 ppm
Alcohol-benzene extractable AOX	15.0 ppm
Unextractable organochlorine	137.0 ppm

This example shows that pulps bleached by the sequence ODED achieve very high brightness using a low level of chlorine dioxide. The AOX in the untreated effluent in this example is predicted to be approximately 1.1 kg AOX per ton of pulp. The TOX residue in pulp is also quite low compared to other pulps.

Example 16

Sequence E₀DED

Birch/aspen/maple organosolv pulp was treated as in Example 4 with a charge of 4.5% sodium hydroxide and 0.5% MgSO₄. Oxygen was mixed with the pulp at 50 psig. Over the next 6 minutes the oxygen pressure was gradually released until the oxygen pressure was atmospheric. The pulp remained in the mixer at 60°C for another 45 minutes, with occasional stirring at low speed. The oxygen delignified pulp was then treated with chlorine dioxide and alkaline extraction as in Example 14 using 2.67% chlorine dioxide in the first bleaching stage.

The results are shown below:

	Kappa No.	Viscosity (cps)	Brightness (ISO)
1. Organosolv Brownstock	39.7	—	—
2. Oxygen Extraction (E_o)	22.3	27.2	—
3. Oxygen Extraction + 1st ClO ₂ Stage + Alkaline Extraction + 2nd ClO ₂ Stage	—	19.0	91

As can be readily seen, an organosolv pulp can be delignified with the milder oxidative extraction (E_o) and still achieve a high brightness of 91 ISO.

5 Example 17

Sequence Z

Birch/maple/aspen organosolv pulp was acidified with sulfuric acid to a pH of about 2 to 3 and then
10 fluffed. The fluffed acidified pulp was contacted with ozone at about 1.3% (w/w) ozone on oven dried (o.d.) pulp, the ozone being present in oxygen as a gas phase carrier. The pulp mixture was agitated during ozonation.

	Kappa No.	Brightness (ISO)
1. Organosolv Brownstock	20.7	—
2. 1.3% Ozone	6.6	48.3

20 As can be readily seen, with a single ozone stage the kappa number is reduced by about 68%.

Example 18

Sequence OZ

25 Birch/maple/aspen organosolv pulp was delignified with oxygen to a kappa number of 9.9 using the conditions of Example 1. The delignified pulp was treated with 0.5% ozone as in Example 17. After ozone treatment, the pulp pH was adjusted to 11 using NaOH. After adjustment with NaOH, the pulp was washed with water to a neutral pH.

	Kappa No.	Brightness (ISO)
1. Organosolv Brownstock	35	—
2. Oxygen Delignification	9.9	—
3. Oxygen Delignification + 0.5% Ozone	2.0*	65.6

* A 25 ml permanganate number can be used as an indication of lignin content when the kappa number is low. As a rough estimate, the kappa number is approximately 1.5 times the permanganate number.

40 As can be readily seen, using an oxygen delignification followed by an ozone stage, the kappa number can be reduced by 90% and the brightness achieved is above 65 ISO.

Example 19

45 Sequence OZ(edta)P, OZ(PA) OZ(edta)PD, OZ(PA)D

Birch/maple/aspen organosolv pulp was delignified with oxygen and treated with ozone as in Example 18. The pulp was then treated with about 0.5% EDTA for 90 minutes at 70°C. The final pH was about 5 to 7. The EDTA treated pulp at 12% consistency was treated with hydrogen peroxide at about 2%. DTPA was added at about 0.2%, at 70°C and for 3 hours. The peroxide treated pulp was further treated with 0.2% chlorine dioxide at 70°C, for 3 hours. Enough NaOH was added to a final pH of 3.5 to 4.5.

Birch/maple/aspen organosolv pulp was delignified with oxygen and treated with ozone as in Example 18. The pulp was then treated with about 2% peracetic acid at a 12% consistency. Enough NaOH was added to a pH of about 5 to 7. DTPA was added at about 0.2% and the reaction proceeded for about 3 hours at 70°C. The peracetic acid treated pulp was further treated with 0.2% chlorine dioxide at 70°C, for 3 hours. Enough NaOH was added to a final pH of 3.5 to 4.5.

		<u>Kappa No.</u>	<u>Brightness (ISO)</u>
5	1. Organosolv brownstock	35	—
	2. Oxygen delignification	9.9	—
10	3. Oxygen delignification + 0.5% Ozone	2.0*	65.6
15	4. Oxygen delignification + 0.5% Ozone + 0.5% EDTA	—	81.1
20	+ 2% hydrogen peroxide	—	
25	5. Oxygen delignification + 0.5% ozone + 2% peracetic acid	—	84.1
30	6. Oxygen Delignification + 0.5% Ozone + 0.5% EDTA	—	
35	+ 2% Hydrogen Peroxide + 0.2% ClO ₂	—	89.1
40	7. Oxygen Delignification + 0.5% Ozone + 2% peracetic acid + 0.2% ClO ₂	—	89.6
45			

* A 25 ml permanganate number can be used as an indication of lignin content when the kappa number is low. As a rough estimate, the kappa number is approximately 1.5 times the permanganate number.

This example shows that an organosolv pulp can be brightened to above 89 ISO with low level chlorine dioxide.

As can be readily seen, a brightness of above 84 ISO can be achieved without the addition of chlorine dioxide. Such pulps will contain zero level TOX from chlorine based bleaching chemicals and correspondingly the bleach effluents contain zero level AOX.

Example 20Sequence ZO

- 5 Maple/aspen/birch organosolv pulp was treated with 0.5% ozone as in Example 17 then delignified with oxygen using the conditions of Example 1.

	Kappa No.	Brightness (ISO)
10 1. Organosolv Brownstock	20.7	—
2. 0.5% Ozone	6.6	48.3
3. 0.5% Ozone + Oxygen Delignification	4.2	58.3

- 15 This example shows that an ozone stage can further delignify a pulp before and after an oxygen delignification stage. A reduction in kappa number of about 80% can be achieved.

Example 21Sequence ZO(edta)P

- 20 Maple/aspen/birch organosolv pulp was treated as in Example 20. The pulp was then treated with hydrogen peroxide. The hydrogen peroxide step is carried out by mixing 2.5% hydrogen peroxide, NaOH to an end pH of 10, at 70°C and for 3 hours. EDTA was added at about 0.5% at about 10 to 12% consistency, for 90 minute and at 70°C.

- 25 The results are shown below:

	Kappa No.	Brightness (ISO)
30 1. Organosolv Brownstock	20.7	—
2. 0.5% Ozone	6.6	48.3
3. 0.5% Ozone + Oxygen Delignification	4.2	58.3
4. 0.5% Ozone + Oxygen Delignification + 0.5% EDTA + 2.5% hydrogen peroxide	—	86

- 35 This example shows that a brightness of about 86 ISO can be achieved with one ozone stage followed by oxygen delignification and an hydrogen peroxide stage. Such organosolv pulps bleached to about 86 ISO without chlorine dioxide will contain zero level TOX from chlorine based bleaching chemicals and correspondingly the bleach effluents contain zero level AOX.

Example 22Sequence OZD

- 45 The organosolv pulp of Example 18 was bleached with chlorine dioxide as in Example 8.

	Kappa No.	Brightness (ISO)
50 1. Organosolv Brownstock	35	65.6
2. Oxygen Delignification	9.9	
3. Oxygen Delignification + 0.5% Ozone	2.0*	65.6
4. Oxygen Delignification + 0.5% ozone + 0.8% ClO ₂	—	89
5. Oxygen Delignification + 0.5% ozone + 0.4% ClO ₂ + 0.4% ClO ₂	—	90

- 55 * A 25 ml permanganate number used as an indication of lignin content when the kappa number is low. As a rough estimate, the kappa number is approximately 1.5 times the permanganate number.

As can be readily seen, a small amount of chlorine dioxide in one stage or two consecutive stages improved the brightness to 90 ISO.

The following example sets forth the continuous delignification and bleaching of a mixture of organosolv and softwood kraft brownstock pulp.

Example 23

Sequence E_oDE_pD

This example illustrates continuous delignification and bleaching with countercurrent recycle of bleaching filtrates. During the stages of delignification and bleaching, the pulp was washed using bleaching filtrates of a subsequent treatment stage.

A mixed brownstock pulp of about 11% to 15% consistency containing 80% birch organosolv pulp and 20% Kraft brownstock pulp was delignified and bleached using the E_oDE_pD stage. In the (E_o) stage, the mixed pulp was treated in an oxidative extraction stage as in Example 4 using a sodium hydroxide charge of about 3.2%. After oxidative extraction, the pulp was washed from filtrates of the (E_p) stage. In a next stage, the mixed pulp was treated with a first chlorine dioxide stage at about 3% (w/w) of chlorine dioxide on oven dried (o.d.) pulp under conditions similar to Example 14. The chlorine dioxide bleached pulp was washed with bleaching filtrates from the second chlorine dioxide bleaching stage that followed the (E_p) Stage. The chlorine dioxide bleached pulp was subjected to an alkaline extraction stage which included the addition of 0.2% hydrogen peroxide and using the same conditions as in Example 6 with a sodium hydroxide charge of about 0.7%. A second chlorine dioxide stage followed with 1.2% ClO_2 and the pH was adjusted using sodium hydroxide to a range of about 3.5 to 4.5.

The results are shown below:

	Kappa No.	Viscosity (cps)	Brightness (ISO)
1. Brownstock	30	—	—
2. Oxidative Extraction	24	—	—
3. Oxidative Extraction + 1st ClO ₂ Stage + Alkaline Extraction	—	27.5	67
4. Oxidative Extraction + 1st ClO ₂ Stage + Alkaline Extraction + 2nd ClO ₂ Stage	—	21	89

This example illustrates a mill trial using the process as shown in Figure 7. However, in this example, oxidative extraction (E_o) which is a milder delignification treatment was used instead of oxygen delignification. To the alkaline extraction step (E) of Figure 7, a low level of hydrogen peroxide was added in order to enhance the brightness of the bleached pulp. A pulp brightness of 89 ISO was obtained.

It is to be understood that while the invention has been described in conjunction with the preferred specific embodiments thereof, the foregoing description as well as the examples are intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

Claims

1. A process for the oxygen delignification of pulp wherein said pulp residual lignin is decreased in excess of 50% and wherein said pulp viscosity is decreased by no more than about 8 cps.
2. The process of claim 1 wherein said pulp residual lignin is decreased in the range of from about 50% to about 76%.
3. The process of claim 1 wherein said pulp viscosity is decreased by no more than from about 2 to about 5 cps.
4. The process of claim 1 wherein said oxygen delignification is carried by reacting said pulp with from about 2% to about 8% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110° C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes.
5. The process of claim 4 which further comprises pretreating said pulp prior to performing said oxygen delignification with at least one treatment stage using a peroxy compound selected from the group consisting of peracetic acid and hydrogen peroxide.
6. The process of claim 5 wherein said peroxy compound is peracetic acid.
7. The process of claim 6 wherein said peracetic acid is in the range of from about 0.5% to about 4% (w/w) peracetic acid on oven dry pulp.
8. The process of claim 7 wherein said peroxy compound is hydrogen peroxide.
9. The process of claim 8 wherein said hydrogen peroxide is in the range of from about 0.5% to about 4% (w/w) hydrogen peroxide based on oven dry pulp.
10. The process of claim 9 wherein said peroxy treatment stage is preceded by an acid wash stage.
11. The process of claim 10 wherein said acid washing stage comprises bubbling sulfur dioxide gas until said pulp is at a pH of from about 2 to about 3.
12. The process of claim 11 wherein said peroxy treatment stage is preceded by a treatment step with a transition-metal chelating agent said transition metal-chelating agent selected from the group consisting of ethylenediamine tetraacetic acid and diethylene triamine pentaacetic acid.
13. The process of claim 12 wherein said metal-chelating agent is from about 0.05 to about 1% (w/w) metal-chelating agent on oven dry pulp.
14. The process of claim 4 which further comprises treating said oxygen delignified pulp with at least one treatment stage using a peroxy compound selected from the group consisting of peracetic acid and hydrogen peroxide.
15. The process of claim 14 wherein said peroxy compound is peracetic acid.

16. The process of claim 15 wherein said peracetic acid is in the range of from about 0.5% to about 4% (w/w) peracetic acid on oven dry pulp.
17. The process of claim 17 wherein said peroxy compound is hydrogen peroxide.
18. The process of claim 17 wherein said hydrogen peroxide is in the range of from about 0.5% to about 4% (w/w) hydrogen peroxide based on oven dry pulp.
19. The process of claim 18 wherein said peroxy treatment stage is preceded by an acid wash stage.
20. The process of claim 19 wherein said acid washing stage comprises bubbling sulfur dioxide gas until said pulp is at a pH of from about 2 to about 3.
21. The process of claim 14 wherein said peroxy treatment stage is preceded by a treatment step with a transition-metal chelating agent said transition metal-chelating agent selected from the group consisting of ethylenediamine tetraacetic acid and diethylene triamine pentaacetic acid.
22. The process of claim 21 wherein said metal-chelating agent is from about 0.05 to about 1% (w/w) metal-chelating agent on oven dry pulp.
23. The process of claim 14 wherein said peroxy treatment stage is followed with an oxidative extraction stage to further delignify said pulp.
24. The process of claim 23 wherein said oxidative extraction stage is carried by reacting said pulp with from about 2% to about 5% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110° C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes and wherein said pulp is at a consistency of from about 9% to 40% pulp solids.
25. The process of claim 4 which further comprises pretreating said pulp with at least one treatment stage using ozone gas prior to performing said oxygen delignification.
26. The process of claim 25 wherein said ozone treatment stage is carried at a pH of from about 1.5 to 5, at a temperature of from about 20° to about 60° C and wherein said pulp is at a consistency of from about 10% to about 50% pulp solids and said ozone gas is from about 0.2% to 2% (w/w) ozone on oven dried pulp.
27. The process of claim 4 which further comprises treating said oxygen delignified pulp with at least one treatment stage using ozone gas.
28. The process of claim 27 wherein said ozone treatment stage is carried at a pH of from about 1.5 to 5, at a temperature of from about 20° to about 60° C and wherein said pulp is at a consistency of from about 10% to about 50% pulp solids and said ozone gas is from about 0.2% to 2% (w/w) ozone on oven dried pulp.
29. The process of claim 27 wherein said ozone treatment stage is followed with an oxidative extraction stage to further delignify said pulp.
30. The process of claim 29 wherein said oxidative extraction stage is carried by reacting said pulp with from about 2% to about 5% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110° C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes and wherein said pulp is at a consistency of from about 9% to 40% pulp solids.
31. The process of claim 4 wherein said oxygen delignification is followed by at least one chlorine dioxide treatment stage.
32. The process of claim 31 wherein said chlorine dioxide treatment stage is carried by reacting said pulp with from about 0.2% to about 1.5% (w/w) chlorine dioxide on oven dry pulp, at a pH of from about 2 to 3 at a temperature of from about 30° to 70° C for a reaction time of from about 0.3 to 2 hours and

wherein said pulp is at a consistency of from 9% to about 15% pulp solids.

33. The process of claim 25 wherein said ozone treatment stage is followed with an oxidative extraction stage to further delignify said pulp.

34. The process of claim 33 wherein said oxidative extraction stage is carried by reacting said pulp with from about 2% to about 5% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110°C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes and wherein said pulp is at a consistency of from about 9% to 40% pulp solids.

35. The process of claim 14 wherein said peroxy treatment stage is followed by at least one chlorine dioxide treatment stage.

36. The process of claim 35 wherein said chlorine dioxide treatment stage is carried by reacting said pulp with from about 0.2% to about 1.5% (w/w) chlorine dioxide on oven dry pulp, at a pH of from about 2 to 3 at a temperature of from about 30° to 70°C for a reaction time of from about 0.3 to 2 hours and wherein said pulp is at a consistency of from 9% to about 15% pulp solids.

37. The process of claim 36 wherein said chlorine dioxide treatment stage is followed with an oxidative extraction stage to further delignify said pulp.

38. The process of claim 37 wherein said oxidative extraction stage is carried by reacting said pulp with from about 2% to about 5% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110°C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes and wherein said pulp is at a consistency of from about 9% to 40% pulp solids.

39. The process of claim 25 wherein said ozone treatment stage is followed by at least one chlorine dioxide treatment stage.

40. The process of claim 39 wherein said chlorine dioxide treatment stage is carried by reacting said pulp with from about 0.2% to about 1.5% (w/w) chlorine dioxide on oven dry pulp, at a pH of from about 2 to 3 at a temperature of from about 30° to 70°C for a reaction time of from about 0.3 to 2 hours and wherein said pulp is at a consistency of from 9% to about 15% pulp solids.

41. A continuous process for the delignification and bleaching of pulp wherein said pulp residual lignin is decreased in excess of 50% and wherein said pulp viscosity is decreased by no more than about 8 cps which comprises the steps of:

(1) treating said pulp at a consistency of from about 10% to about 15% pulp solids with at least one peroxy compound said peroxy compound selected from the group consisting of hydrogen peroxide and peracetic acid and said peroxy compound at from about 0.2% to 2% (w/w) peroxy compound on oven dried pulp at a final pH of from about 8.5 to about 11 at a temperature of from about 40° to 90°C and for a reaction time of from about 0.3 to about 3 hours;

(2) oxygen delignifying said peroxy treated pulp with from about 2% to about 8% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110°C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes;

(3) treating said oxygen delignified pulp at a consistency of from about 10% to about 12% pulp solids with at least one peroxy compound said peroxy compound selected from the group consisting of hydrogen peroxide and peracetic acid and said peroxy compound at from about 0.2% to 2% (w/w) peroxy compound on oven dried pulp at a final pH of from about 8.5 to about 11 at a temperature of from about 40° to 90°C and for a reaction time of from about 0.3 to about 3 hours.

42. A continuous process for the delignification and bleaching of pulp wherein said pulp residual lignin is decreased in excess of 50% and wherein said pulp viscosity is decreased by no more than about 8 cps which comprises the steps of:

(1) treating said pulp at a consistency of from about 10% to about 15% pulp solids with at least one peroxy compound said peroxy compound selected from the group consisting of hydrogen peroxide and peracetic acid and said peroxy compound at from about 0.2% to 2% (w/w) peroxy compound on oven dried pulp at a final pH of from about 8.5 to about 11 at a temperature of from about 40° to

90° C and for a reaction time of from about 0.3 to about 3 hours;

(2) oxygen delignifying said peroxy treated pulp with from about 2% to about 8% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110° C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes;

5 (3) treating said oxygen delignified pulp at a consistency of from about 20% to about 50% pulp solids with ozone gas at a pH of from about 1.5 to 5, at a temperature of from about 20° to about 60° C and wherein said ozone gas is from about 0.2% to 2% (w/w) ozone on oven dried pulp.

10 (4) treating said ozone treated pulp at a consistency of from about 10% to about 12% pulp solids with at least one peroxy compound said peroxy compound selected from the group consisting of hydrogen peroxide and peracetic acid and said peroxy compound at from about 0.2% to 2% (w/w) peroxy compound on oven dried pulp at a final pH of from about 8.5 to about 11 at a temperature of from about 40° to 90° C and for a reaction time of from about 0.3 to about 3 hours.

15 43. A continuous process delignification and bleaching of pulp wherein said pulp residual lignin is decreased in excess of 50% and wherein said pulp viscosity is decreased by no more than about 8 cps which comprises the steps of:

(1) oxygen delignifying said peroxy treated pulp with from about 2% to about 8% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110° C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes;

20 (2) treating said oxygen delignified pulp at a consistency of from about 10% to about 12% pulp solids with at least one peroxy compound said peroxy compound selected from the group consisting of hydrogen peroxide and peracetic acid and said peroxy compound at from about 0.2% to 2% (w/w) peroxy compound on oven dried pulp at a final pH of from about 8.5 to about 11 at a temperature of from about 40° to 90° C and for a reaction time of from about 0.3 to about 3 hours

25 (3) treating said peroxy treated pulp with chlorine dioxide by reacting said pulp with from about 0.2% to about 1.5% (w/w) of said chlorine dioxide on oven dry pulp, at a pH of from about 2 to 3 at a temperature of from about 30° to 70° C for a reaction time of from about 0.3 to 2 hours and wherein said pulp is at a consistency of from 9% to about 15% pulp solids.

30 44. A continuous process delignification and bleaching of pulp wherein said pulp residual lignin is decreased in excess of 50% and wherein said pulp viscosity is decreased by no more than about 8 cps which comprises the steps of:

(1) oxygen delignifying said peroxy treated pulp with from about 2% to about 8% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110° C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes;

35 (2) treating said oxygen delignified pulp at a consistency of from about 20% to about 50% pulp solids with ozone gas at a pH of from about 1.5 to 5, at a temperature of from about 20° to about 60° C and wherein said ozone gas is from about 0.2% to 2% (w/w) ozone on oven dried pulp;

40 (3) treating said ozone treated pulp with chlorine dioxide by reacting said ozone treated pulp with from about 0.2% to about 1.5% (w/w) of said chlorine dioxide on oven dry pulp, at a pH of from about 2 to 3 at a temperature of from about 30° to 70° C for a reaction time of from about 0.3 to 2 hours and wherein said pulp is at a consistency of from about 9% to about 15% pulp solids.

45 45. A continuous process delignification and bleaching of pulp wherein said pulp residual lignin is decreased in excess of 50% and wherein said pulp viscosity is decreased by no more than about 8 cps which comprises the steps of:

(1) oxygen delignifying said peroxy treated pulp with from about 2% to about 8% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110° C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes;

50 (3) treating said oxygen delignified pulp with chlorine dioxide in a first bleaching stage by reacting said ozone treated pulp with from about 0.2% to about 1.5% (w/w) of said chlorine dioxide on oven dry pulp, at a pH of from about 2 to 3 at a temperature of from about 30° to 70° C for a reaction time of from about 0.3 to 2 hours and wherein said pulp is at a consistency of from about 9% to about 15% pulp solids;

55 (3) treating said first bleached pulp in an oxidative extraction stage with from about 2% to about 5% (w/w) sodium hydroxide on oven dry pulp at a temperature of from about 60° to 110° C at an oxygen pressure of from about 30 to 100 psig and for a reaction time of from about 6 to 60 minutes and wherein said pulp is at a consistency of from about 9% to 40% pulp solids; and

(4) treating said step (3) pulp with chlorine dioxide in a second bleaching stage by reacting said pulp with from about 0.2% to about 1.5% (w/w) of said chlorine dioxide on oven dry pulp, at a pH of from about 2 to 3 at a temperature of from about 30° to 70° C for a reaction time of from about 0.3 to 2 hours and wherein said pulp is at a consistency of from about 9% to about 15% pulp solids.

5

46. A process for the oxygen delignification and bleaching of pulp wherein said pulp residual lignin is decreased in excess of 50% and wherein said pulp viscosity is decreased by no more than about 8 cps said pulp having a total TOX level of up to 200 ppm from chlorine based bleaching chemicals.

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47. Wood pulp having a total TOX level of up to 200 ppm from chlorine based bleaching chemicals.

48. The wood pulp of claim 47 wherein the brightness of said pulp is 91 ISO.

49. The wood pulp of claim 47 having zero level TOX from chlorine based bleaching chemicals.

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50. The wood pulp of claim 49 wherein the brightness of said pulp is from about 83 to about 86 ISO.

51. The process of claim 1 wherein said pulp is organosolv pulp.

20

52. The process of claim 4 wherein said pulp is organosolv pulp.

53. The process of claim 14 wherein said pulp is organosolv pulp.

54. The process of claim 23 wherein said pulp is organosolv pulp.

25

55. The process of claim 25 wherein said pulp is organosolv pulp.

56. The process of claim 27 wherein said pulp is organosolv pulp.

30

57. The process of claim 29 wherein said pulp is organosolv pulp.

58. The process of claim 31 wherein said pulp is organosolv pulp.

35

59. A bleached pulp by the process of claim 5 wherein the brightness of said pulp is from about 52 to about 83 ISO.

60. A bleached pulp by the process of claim 14 wherein the brightness of said pulp is from about 52 to about 83 ISO.

40

61. A bleached pulp by the process of claim 25 wherein the brightness of said pulp is about 86 ISO.

62. A bleached pulp by the process of claim 27 wherein the brightness of said pulp is from about 65 to 85 ISO.

45

63. A bleached pulp by the process of claim 31 wherein the brightness of said pulp is from about 89 to 91 ISO.

64. A bleached pulp by the process of claim 41 wherein the brightness of said pulp is from about 83 to 88 ISO.

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65. A bleached pulp by the process of claim 42 wherein the brightness of said pulp is from about 83 to 88 ISO.

55

66. A bleached pulp by the process of claim 43 wherein the brightness of said pulp is from about 90 to 92 ISO.

67. A bleached pulp by the process of claim 44 wherein the brightness of said pulp is from about 90 to 92 ISO.

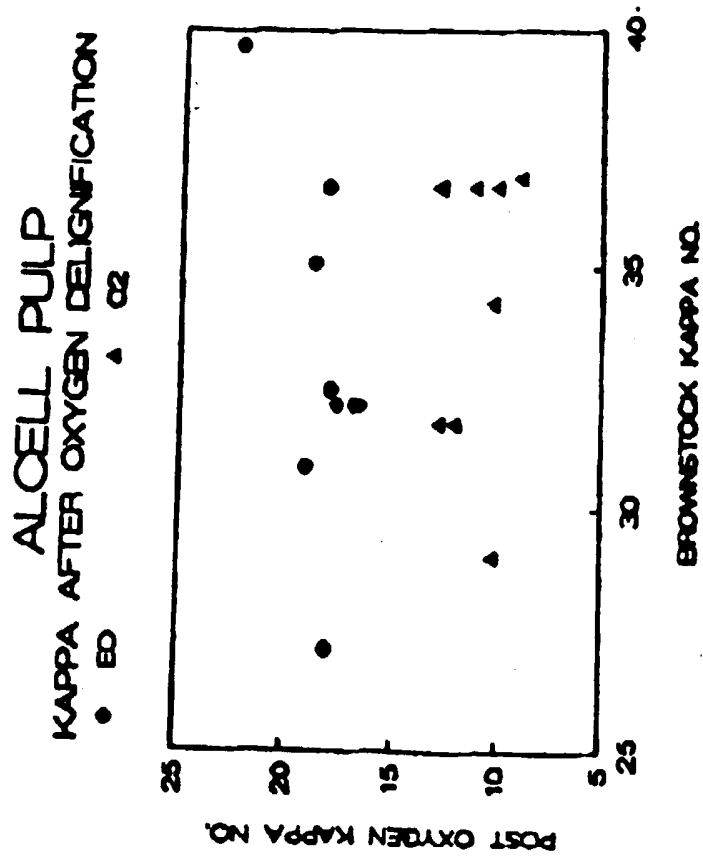


FIGURE 1

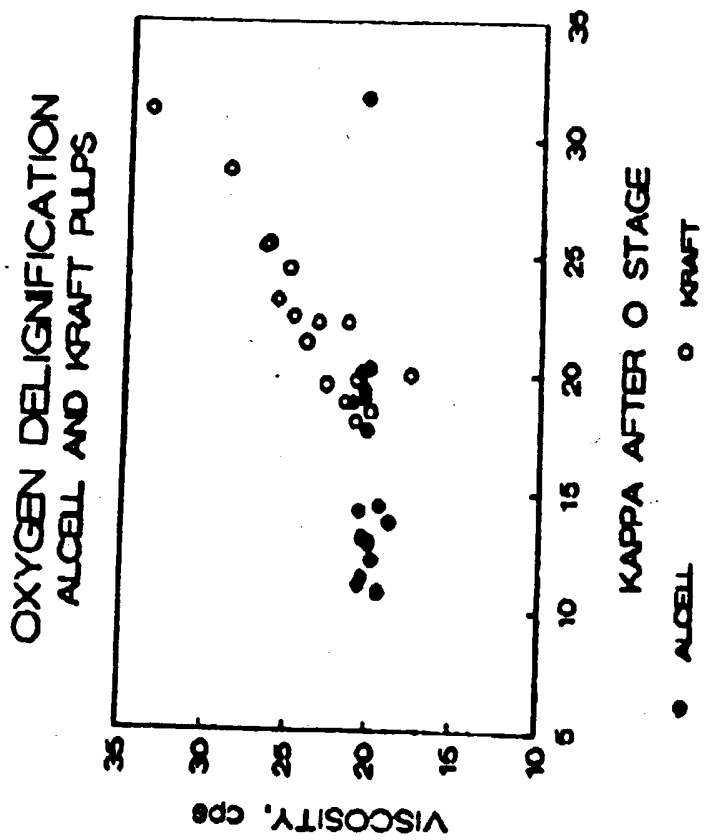


FIGURE 2

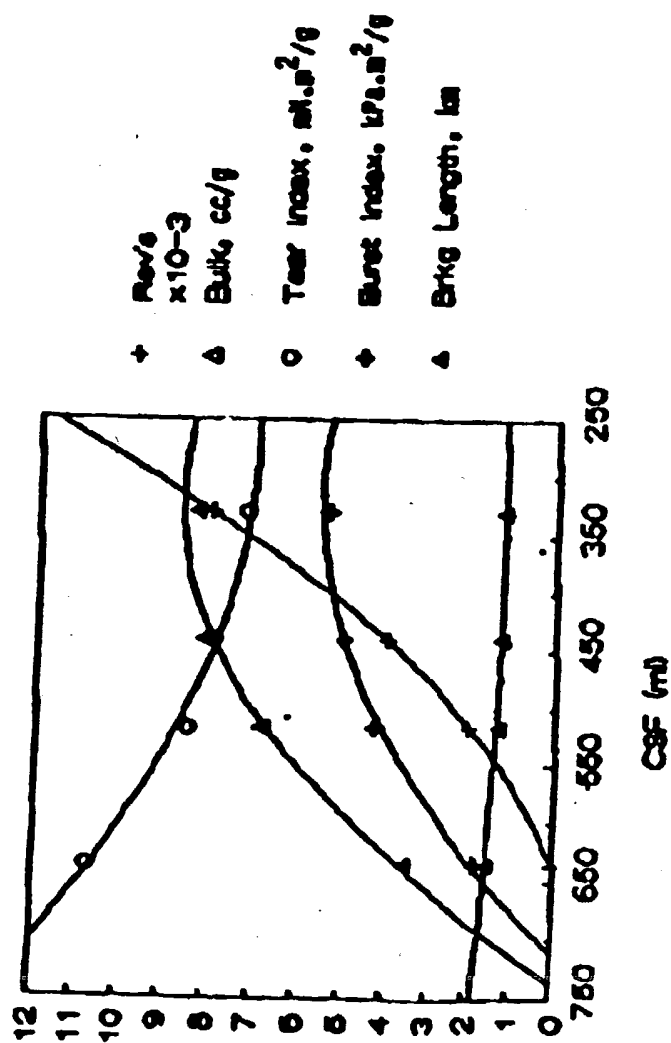


FIGURE 3

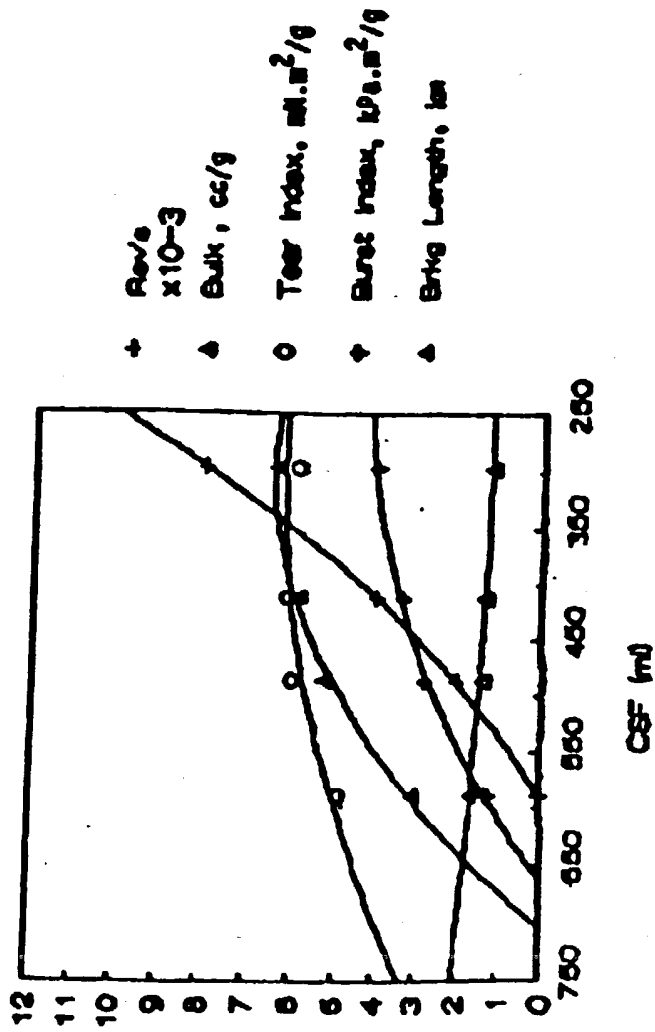


FIGURE 4

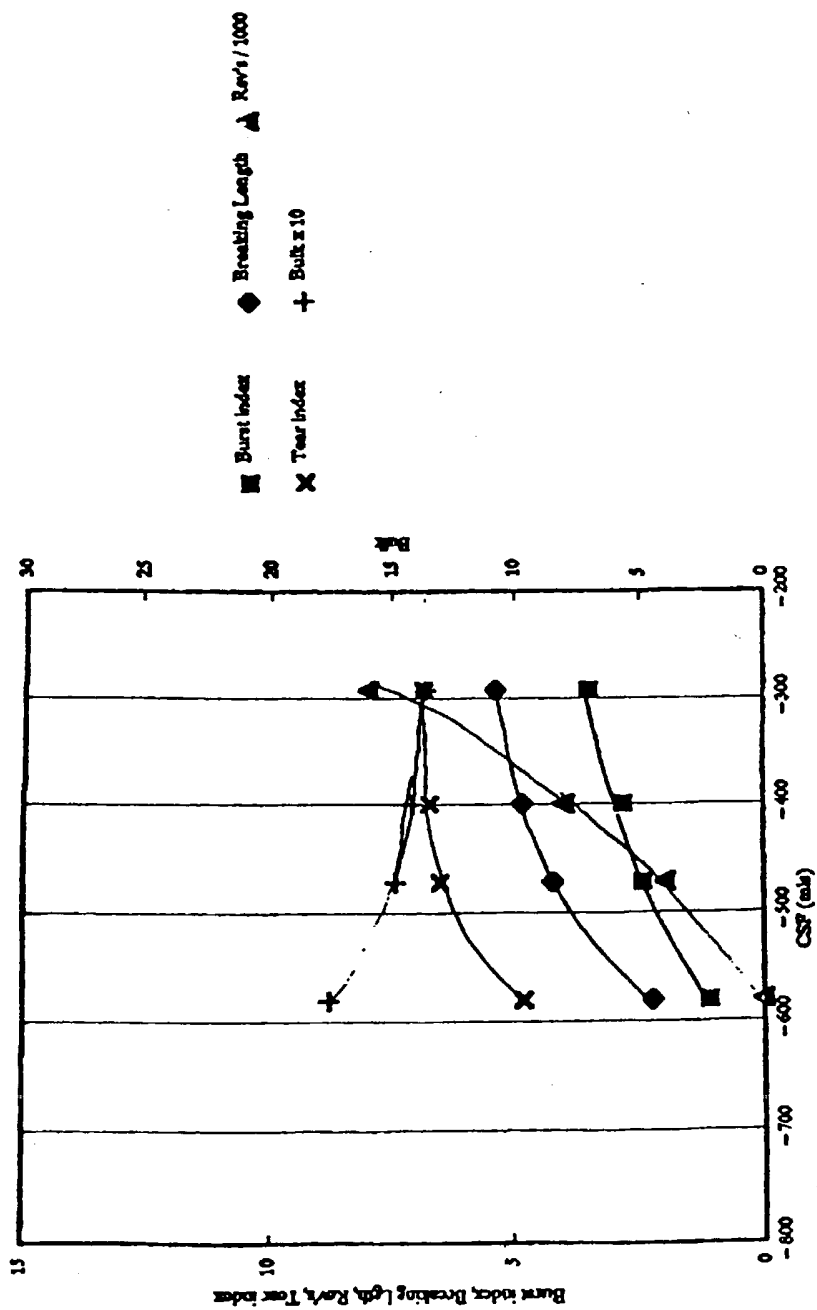


FIGURE 5

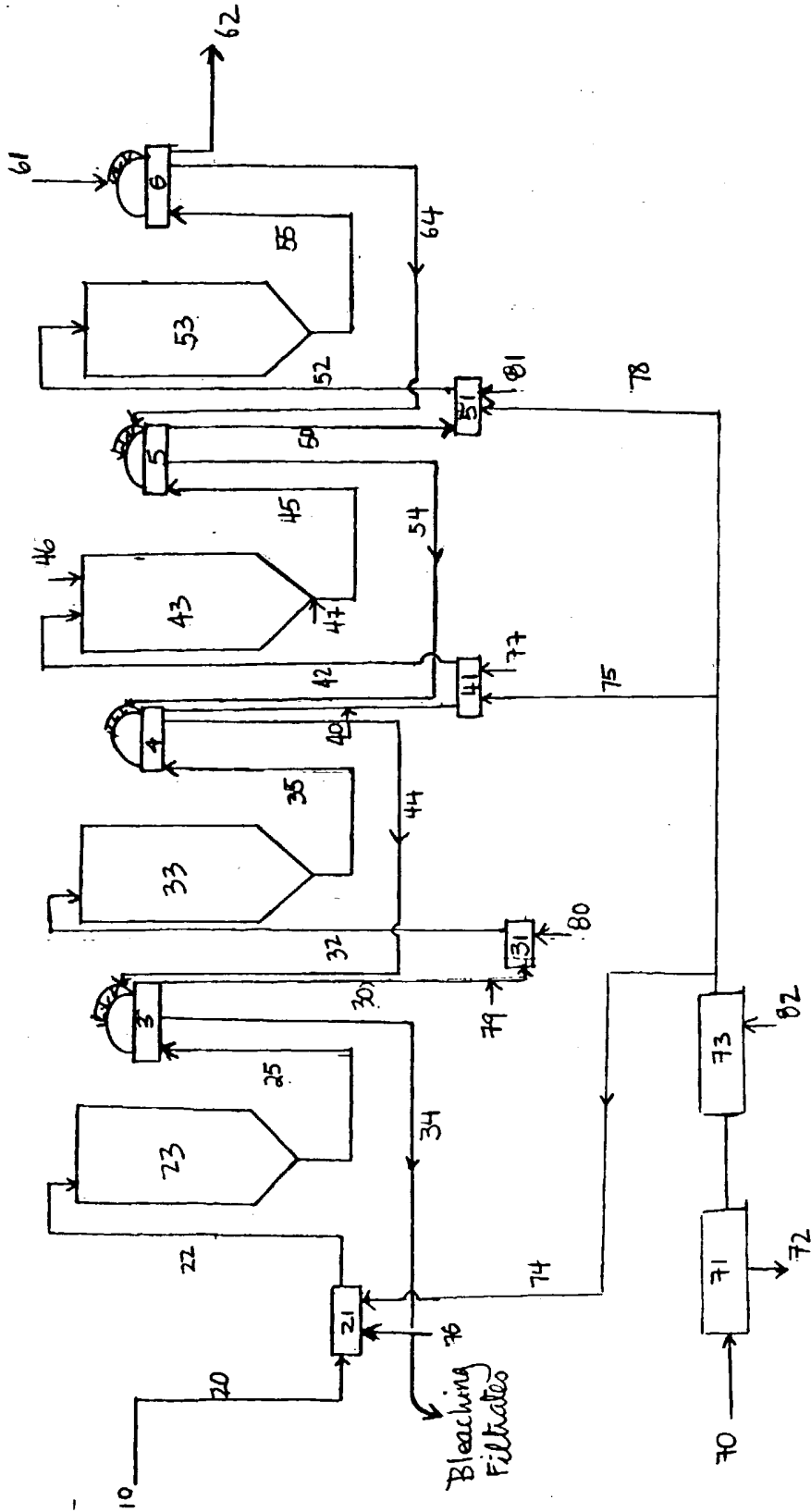


FIGURE 6

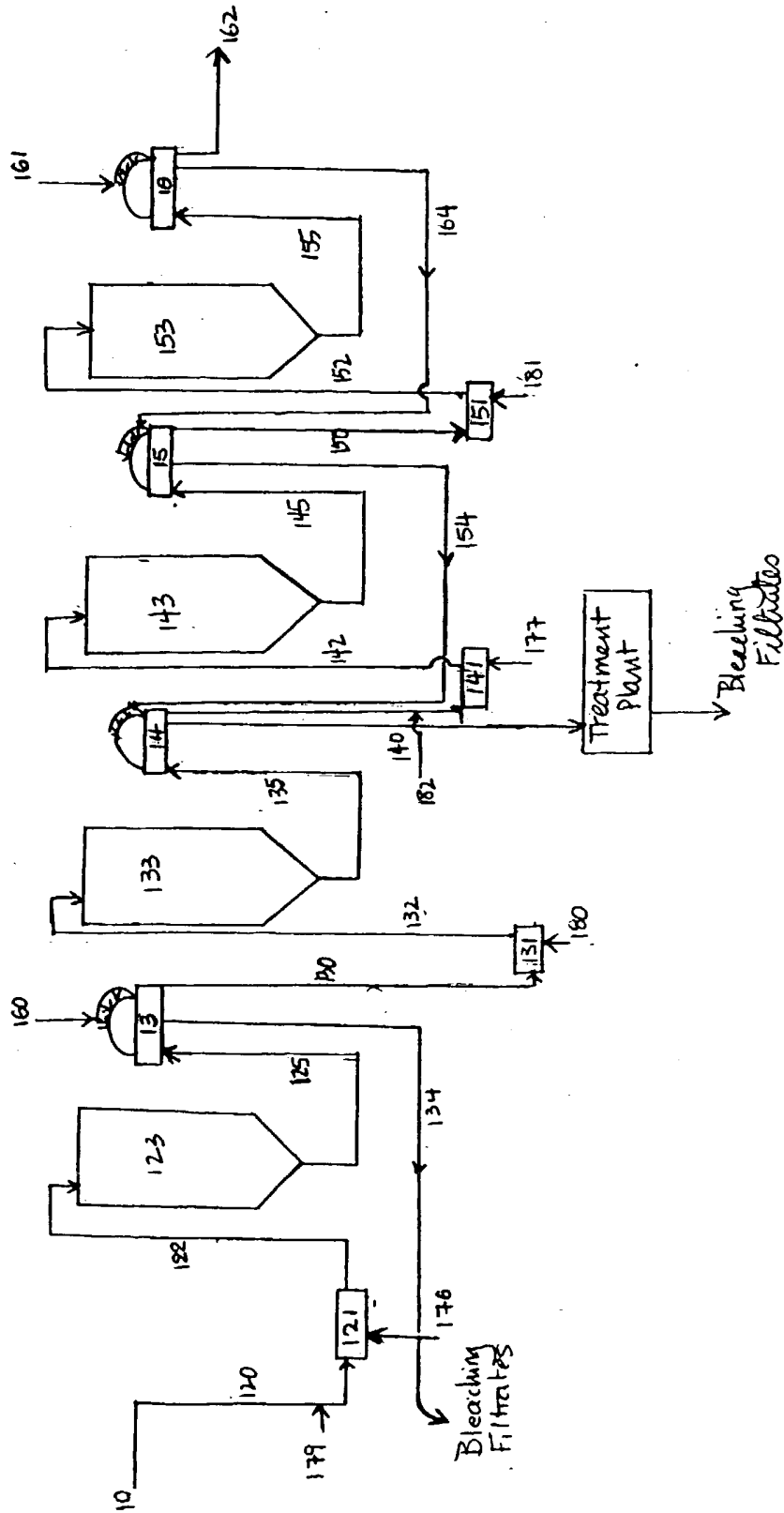


FIGURE 7

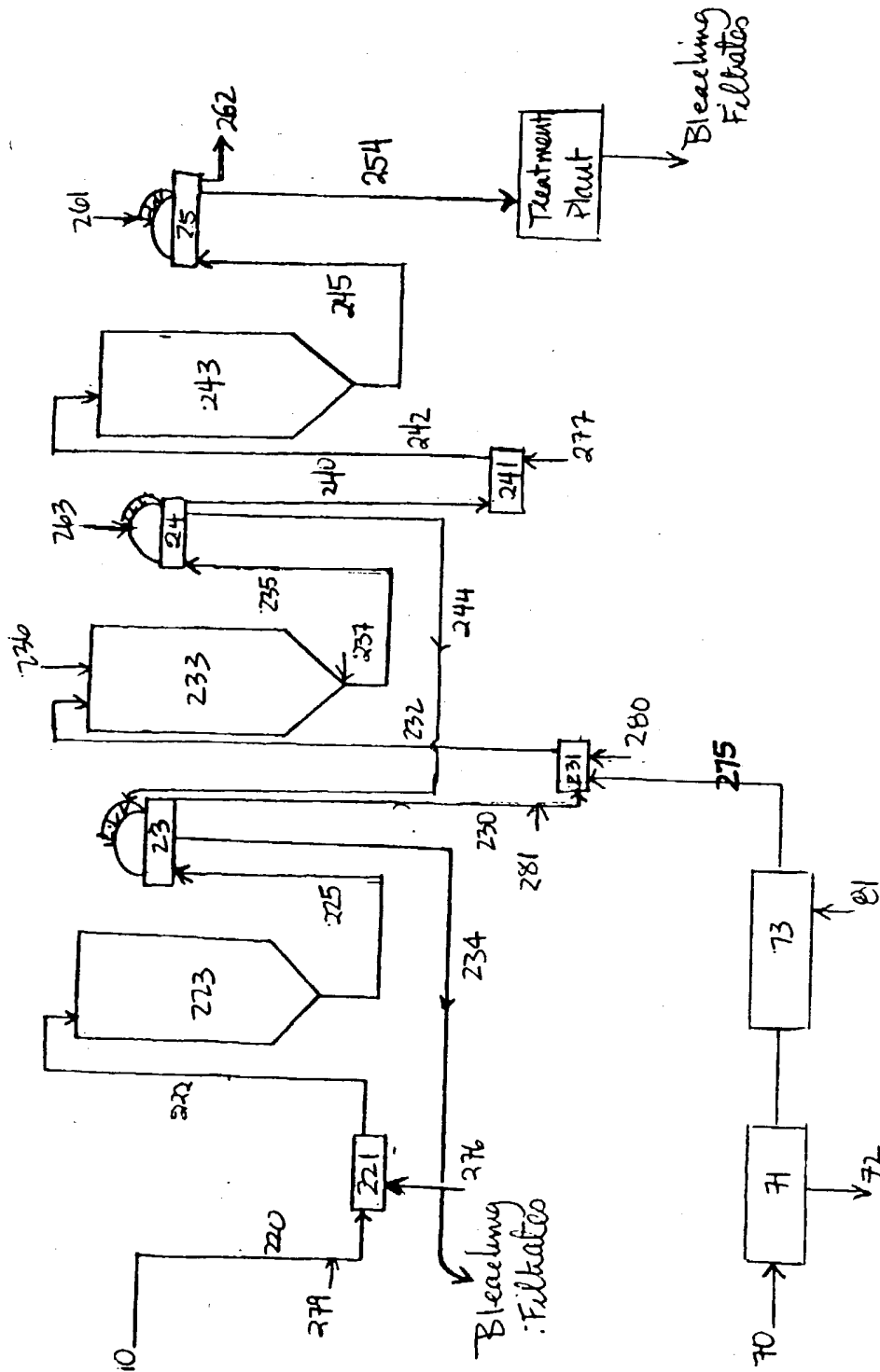


FIGURE 8